

U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB-294 741

Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units

Radian Corp, Austin, TX

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, NC

Feb 79

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/2-79-044	2.	3. REF PB294741
4. TITLE AND SUBTITLE Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units		5. REPORT DATE February 1979
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Robert Wetherold and Lloyd Provost		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation P.O. Box 9948 Austin, Texas 78766		10. PROGRAM ELEMENT NO. 1AB604
		11. CONTRACT/GRANT NO. 68-02-2147 and -2665
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Interim; 3/76 - 3/79
		14. SPONSORING AGENCY CODE EPA/600/13
15. SUPPLEMENTARY NOTES IERL-RTP project officer is Dale A. Denny, MD-62, 919/541-2547		
16. ABSTRACT The report gives results of sampling fugitive emissions at nine integrated oil refineries throughout the U.S. The petroleum refining industry is a significant source of atmospheric hydrocarbon (HC) emissions in the U.S. Each refinery has a large number of potential emission sources, both controlled (e.g., stacks and vents) and uncontrolled (e.g., leaks). HC emission data were collected for valves, flanges, pump and compressor seals, pressure relief valves, and process drains. The sampling techniques are presented. Potential leaking components were initially screened using portable HC detectors; screened devices which indicate significant emissions were then subjected to fully qualitative and quantitative sampling and analysis. For the nine refineries, 5680 sources were screened, 1250 of which were sampled and analyzed. Data on non-methane HC emission rates are presented for each fugitive source, with statistics on data variability. Information on frequency of leaks is also provided. These data show that most HC emissions from fugitive sources occur due to a relatively few leaking components. Gas/vapor streams contribute a proportionately greater amount of emissions than the light and heavy liquid streams.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Sampling Petroleum Refining Analyzing Hydrocarbons Leakage Flue Gases Vents	Pollution Control Stationary Sources Fugitive Emissions Nonmethane Hydrocarbons	13B 13H 07C 14B 21B 13A
18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS (This Report) Unclassified 20. SECURITY CLASS (This page) Unclassified	21. NO. OF PAGES 78 22. PRICE A05-A01

PB 294741

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/2-79-044
February 1979

Research and Development



Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units

REPRODUCED BY
**NATIONAL TECHNICAL
INFORMATION SERVICE**
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

EPA REVIEW NOTICE

This report has been reviewed by the U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policy of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/2-79-044

February 1979

Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units

by

Robert Wetherold and Lloyd Provost

Radian Corporation
P.O. Box 9948
Austin, Texas 78766

Contract Nos. 68-02-2147 and 68-02-2665
Program Element No. 1AB604

EPA Project Officer: Dale A. Denny

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

i. a

ACKNOWLEDGMENT

Mr. C. D. Smith and Dr. D. D. Rosebrook of Radian Corporation are also co-authors of this report.

The authors wish to acknowledge the assistance of Dr. Dale Denny, Dr. I. A. Jefcoat, and Dr. Bruce Tichenor of the Environmental Protection Agency under whose guidance this program has been carried out.

We wish to thank the members of the Ad Hoc Advisory Panel of the American Petroleum Institute. Their assistance in the formulation of the program and their advice during its duration are greatly appreciated. The authors especially wish to thank Mr. Edward P. Crockett of the American Petroleum Institute for his considerable efforts in support of the project.

We are grateful to Mr. Herbert W. Bruch of the National Petroleum Refiners Association for his substantial assistance in this program.

The data upon which this report is based were obtained at a number of refineries throughout the country. The assistance and exceptional cooperation of the staffs of these refineries is gratefully acknowledged.

It would be impossible to individually thank everyone on the Radian staff who participated in this program. Their outstanding attitude and dedication have made this project successful.

TABLE OF CONTENTS

	<u>Page</u>
List of Figures	iv
List of Tables	vii
Section 1 - Executive Summary	1
Section 2 - Introduction	4
Section 3 - Program Design and Source Selection	5
Section 4 - Results of Screening and Sampling Program	11
Appendix A - Emission Factor Development - Statistical Considerations	
References	

LIST OF FIGURES

	<u>Page</u>
Figure 4-1. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Valves and Flanges - Gas/Vapor Streams - Part I	13
Figure 4-2. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Valves and Flanges - Gas/Vapor Streams - Part II	14
Figure 4-3. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Valves and Flanges - Light Liquid/Two-Phase and Heavy Liquid Streams Part I	15
Figure 4-4. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Valves and Flanges - Light Liquid/Two-Phase and Heavy Liquid Streams Part II.	16
Figure 4-5. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Pumps, Compressors, Drains, Relief Valves - Part I	17
Figure 4-6. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Pumps, Compressors, Drains, Relief Valves - Part II	18
Figure 4-7A. Cumulative Distribution of Total Emissions by Screening Values - Valves - Gas/Vapor Streams	28
Figure 4-7B. Cumulative Distribution of Sources by Screening Values - Valves - Gas/Vapor Streams	29
Figure 4-8A. Cumulative Distribution of Total Emissions by Screening Values - Valves - Light Liquid/Two-Phase Streams	30
Figure 4-8B. Cumulative Distribution of Sources by Screening Values - Valves - Light Liquid/Two-Phase Streams.	31
Figure 4-9A. Cumulative Distribution of Total Emissions by Screening Values - Valves - Heavy Liquid Streams	32
Figure 4-9B. Cumulative Distribution of Sources by Screening Values - Valves - Heavy Liquid Streams.	33

	<u>Page</u>
Figure 4-10A. Cumulative Distribution of Total Emissions by Screening Values - Pump Seals - Light Liquid Streams	34
Figure 4-10B. Cumulative Distribution of Sources by Screening Values - Pump Seals - Light Liquid Streams.	35
Figure 4-11A. Cumulative Distribution of Total Emissions by Screening Values - Pump Seals - Heavy Liquid Streams	36
Figure 4-11B. Cumulative Distribution of Sources by Screening Values - Pump Seals - Heavy Liquid Streams.	37
Figure 4-12A. Cumulative Distribution of Total Emissions by Screening Values - Compressor Seals - Hydrocarbon Service.	38
Figure 4-12B. Cumulative Distribution of Sources by Screening Values - Compressor Seals - Hydrocarbon Service	39
Figure 4-13A. Cumulative Distribution of Total Emissions by Screening Values - Compressor Seals - Hydrogen Service	40
Figure 4-13B. Cumulative Distribution of Sources by Screening Values - Compressor Seals - Hydrogen Service.	41
Figure 4-14A. Cumulative Distribution of Total Emissions by Screening Values - Flanges	42
Figure 4-14B. Cumulative Distribution of Sources by Screening Values - Flanges.	43
Figure 4-15A. Cumulative Distribution of Total Emissions by Screening Values - Drains.	44
Figure 4-15B. Cumulative Distribution of Sources by Screening Values - Drains	45
Figure 4-16A. Cumulative Distribution of Total Emissions by Screening Values - Relief Valves	46
Figure 4-16B. Cumulative Distribution of Sources by Screening Values - Relief Valves.	47
Figure A-1. Valves and Flanges - Leak Rate/Screening Relationship - Gas/Vapor Streams	A-9
Figure A-2. Valves and Flanges - Leak Rate/Screening Relationship - Light Liquid/Two-Phase and Heavy Liquid Streams.	A-10

Figure A-3.	Pumps, Compressors, Drains, Relief Valves - Leak vs Screening - All Process Streams.	A-11
Figure A-4.	Distribution of Log_{10} (Max Screening Value)-Valves - Gas/Vapor Streams	A-13
Figure A-5.	Cumulative Distribution of Total Emissions by Screening Values - Valves - Light Liquid/Two-Phase Streams - Comparison of Confidence Intervals	A-17

LIST OF TABLES

	<u>Page</u>
Table 1-1. Estimated Vapor Emission Factors for Nonmethane Hydrocarbons from Selected Sources	2
Table 3-1. Process Units Sampled in Nine Refineries	6
Table 3-2. Range of Choice Variables for Screened Baggable Sources	7
Table 3-3. Process Stream Classification by Group.	9
Table 4-1. Confidence Intervals for Mean and Individual Leak Rates - Valves and Flanges - Gas/Vapor Streams	19
Confidence Intervals for Mean and Individual Leak Rates - Valves and Flanges - Light Liquid/Two-Phase and Heavy Liquid Streams	20
Confidence Intervals for Mean and Individual Leak Rates - Pump Seals, Compressor Seals, Drains, Relief Valves - All Process Stream Types	21
Table 4-2. Summary Statistics and Estimated Vapor Emission Factors for Nonmethane Hydrocarbons from Baggable Sources	22
Table 4-3. Hypothetical Refinery - Based on ADL Texas Gulf Cluster Model (330,000 BPCD)	25
Table 4-4. Distribution of Measured Leak Rates	26
Table 4-5. Percent of Total Mass Emissions Released by the Upper Ten Percent of Screened Sources	49
Table A-1. Prediction Equations for Nonmethane Leak Rates Based on Maximum TLV Screening or Rescreening Values.	A-2

SECTION 1

EXECUTIVE SUMMARY

For the past three years, the Environmental Protection Agency has been sponsoring a petroleum refinery assessment program. As part of this program, fugitive hydrocarbon emissions have been measured from a number of types of sources in refineries. This report has been prepared to distribute some of the data and results obtained thus far in the program. These data should prove to be of value in the development of state and federal regulations involving fugitive hydrocarbon emissions from sources in petroleum refineries.

The results presented in this report have been developed from data obtained at nine refineries throughout the country. The data for compressor seals and relief valves represent thirteen refineries. A wide variety of equipment, process units, and crude oils were included in this study. In this report, the nonmethane hydrocarbon emissions from selected fugitive sources are described. These sources include valves, flanges, pump seals, compressor seals, relief valves, and process drains.

At each refinery, random sample sets of each type of source were selected, "screened", and if necessary, sampled. The "screening" of sources was accomplished with portable hydrocarbon detectors. The "screening values" were defined as the maximum hydrocarbon concentrations detected at the selected source. Extensive data were taken for each of the selected sources.

One of the important results of this study has been the establishment of relationships between the screening values and the measured leak rates of the various sources. Nomographs were developed which relate the predicted mean leak rates to the maximum screening values for the various source types. Confidence intervals for the true mean leak rate are included in the nomographs.

The emission factors for nonmethane hydrocarbon emissions from selected types of sources were developed. These emission factors are summarized in Table 1-1. A very high correlation was found between mass emission rates from sources and the type of stream service in which the sources were employed. Except for compressed gases, streams were classified into one of three stream groups; (1) gas/vapor streams (2) light liquid/two-phase streams, and (3) kerosene and heavier liquid streams. Gases passing through compressors were classified as either hydrogen or hydrocarbon service. It was found that sources in gas/vapor stream service had higher emission rates than those sources in heavier stream service. This trend was especially pronounced for valves and pump seals. Overall emission factors for these two sources are not presented. The distribution of valves and pump seals within the three stream groups must be known or estimated to develop applicable overall process unit and refinery emission factors for these two source types.

TABLE 1-1. ESTIMATED VAPOR EMISSION FACTORS FOR NONMETHANE HYDROCARBONS FROM SELECTED SOURCES

SOURCE TYPE	ESTIMATED PERCENT LEAKING	95% CONFIDENCE INTERVAL FOR PERCENT LEAKING	EMISSION FACTOR ESTIMATE (lb/hr - Source)	95% CONFIDENCE INTERVAL FOR EMISSION FACTOR (lb/hr - Source)
VALVES				
Gas/Vapor Streams	29.3	(25.9 , 32.7)	0.047	(0.027 , 0.064)
Light Liquid/Two-Phase Streams	36.5	(33.6 , 39.5)	0.023	(0.016 , 0.034)
Heavy Liquid Streams	6.7	(4.6 , 8.9)	0.0007	(0.0002 , 0.002)
FLANGES				
	3.1	(2.2 , 3.9)	0.00058	(0.0002 , 0.001)
PUMP SEALS				
Light Liquid Streams	63.8	(58.9 , 68.8)	0.26	(0.17 , 0.39)
Heavy Liquid Streams	22.6	(17.1 , 28.1)	0.045	(0.02 , 0.11)
COMPRESSOR SEALS				
Hydrocarbon Service	70.3	(62.9 , 77.7)	0.98	(0.46 , 2.0)
Hydrogen Service	81.2	(71.2 , 88.8)	0.10	(0.04 , 0.24)
DRAINS				
	19.2	(14.4 , 24.0)	0.070	(0.02 , 0.20)
RELIEF VALVES				
	39.2	(25.1 , 40.6)	0.19	(0.07 , 0.52)

¹Leaking sources in this report are defined as sources with screening values >200 ppmv or sources with measured leak rates greater than 0.00001 lbs/hr.

Emission factors are given for compressor seals in each of the two gas service classifications. The number of seals in each type of service must be known to develop overall process unit or refinery emissions.

Valves, because of their number and relatively high emission factor are the major emission source among the source types discussed in this report. This conclusion is based on an analysis of a hypothetical refinery coupled with the emission rates developed herein.

Nomographs have also been prepared which relate the maximum screening values to the percentage of sources leaking and to the percentage of total emissions represented by these leaking sources. These nomographs can be used to predict the potential maximum* reduction of emissions due to maintenance programs. Data have been collected at four additional refineries to determine the effectiveness of maintenance in reducing fugitive emissions. These data are not discussed in this report, but will be available in the final report for this program.

* Maximum, because the percentages from the nomographs can only be eliminated if maintenance will result in zero emissions for any given source.

SECTION 2

INTRODUCTION

Because of the amount of current activity in the development of state and federal regulations involving fugitive hydrocarbon emissions from refining activities, it is imperative to place available current data in the hands of all concerned parties.

This report has been prepared solely for the purpose of distribution of data. For that reason, only minimal detail has been provided on the experimental and computational aspects of the program. The discussion of the data is also brief pending the development of complete sets of all correlation factors.

The emission factors presented in this report are completely general (i.e., they are neither region nor refinery specific), and for that reason, they have a wider applicability than previously generated data.

SECTION 3

PROGRAM DESIGN AND SOURCE SELECTION

The results presented in this report have been developed from data taken primarily at nine refineries. Data for compressors and relief valves were also obtained at four additional refineries. The refineries were located in major refining areas throughout the country. Large, small, new and old refineries were sampled. Thus, a wide variety of equipment, process units, and crude oils were included in this study.

All of the major refinery processing units were studied in this program. In each refinery, sources in six to nine refinery units were selected for study. The number of each type of process unit sampled are presented in Table 3-1.

In this report, the emissions from "baggage" sources are presented. Baggage sources are those that can be completely enclosed to measure their emission rates. Included in this category are valves, flanges, pump seals, compressor seals, relief valves, and process drains.

Variables which might affect the fugitive emissions from baggage sources were classified as either choice or correlating parameters. A choice parameter is defined as a variable that may directly affect fugitive emissions and is used in selecting the source distribution. These choice parameters for the five types of baggage sources are listed in Table 3-2.

All other variables which might affect the level of fugitive emissions are considered as correlating parameters. The values of all selected correlating variables are recorded for each selected source. The number of correlating parameters ranges from 17 for pumps to 2 for drains.

Obtaining a statistically significant sample population for all combinations of even the choice variables would require a prohibitively large number of samples. Therefore, a sampling plan was devised that required a minimum number of measurements to determine leak rates within the desired accuracies. By assuming that interactions between the variables were unimportant, the number of necessary measurements were reduced. A factorial experimental design procedure was used to select combinations of the variables so that the relationship of each variable with the leak rates could be determined. Regression analysis and analysis of variance were used to determine which variables are significantly related to the leakage. The sampling plans for successive selected refineries were adjusted according to the results from the refineries that had been sampled previously.

The distribution of selected sources in the first six refineries encompassed the full range of choice and correlating variables. One of the most important of the correlating parameters is the type of process stream associated with each of the various selected source types. Hydrocarbon

TABLE 3-1. PROCESS UNITS SAMPLED IN NINE REFINERIES

REFINERY PROCESS UNIT	NUMBER OF SAMPLED UNITS
Atmospheric Distillation	7
Vacuum Distillation	4
Thermal Operations (Coking)	2
Catalytic Cracking	5
Catalytic Reforming	6
Catalytic Hydrocracking	2
Catalytic Hydrorefining	2
Catalytic Hydrotreating	7
Alkylation	6
Aromatics/Isomerization	3
Lube Oil Manufacture	2
Asphalt Manufacture	1
Fuel Gas/Light-Ends Processing	11
LPG	2
Sulfur Recovery	1
Other	3

TABLE 3-2. RANGE OF CHOICE VARIABLES FOR SCREENED BAGGABLE SOURCES

BAGGABLE SOURCE	CHOICE VARIABLE	VARIABLE RANGES FOR SCREENED SOURCES
Valves	Pressure	-10 - 3000 psig
	Temperature	-190 - 925°F
	Fluid State	Gas, Liquid, Two-Phase
	Service	In-line, Open-ended
	Function	Block, Throttling, Control
	Size	0.5 - 36 inches
Flanges	Pressure	-14 - 3000 psig
	Temperature	-30 - 950°F
	Fluid State	Gas, Liquid, Two-Phase
	Service	Pipe, Exchanger, Vessel, Orifice
	Size	1 - 54 inches
Pump Seals	Pressure	0 - 3090 psig
	Temperature	0 - 800°F
	Capacity	0 - 100,000 gpm
	Shaft Motion	Centrifugal, Reciprocating
	Seal Type	Mechanical Seal, Packed Seal
	Liquid RVP	Complete range
Compressor Seals	Pressure	0 - 3000 psig
	Temperature	40 - 300°F
	Capacity	0.06 - 66.0 MMSCFD
	Shaft Motion	Centrifugal, Reciprocating
	Seal Type	Packed, Labyrinth, Mechanical
	Lubrication Method	Hydrocarbon lubricant
Drains	Service	Active, Wash-up
Relief Valves	Pressure	0 - 1350 psig
	Temperature	40 - 1100°F
	Fluid State	Gas, Liquid

stream groups were developed, and all process streams were placed in one of these classifications. Three major stream groups were defined. The three groups and the descriptions of the streams within each group are shown in Table 3-3. The "Gas/Vapor" group contains those hydrocarbon streams which were completely vaporized at the process conditions. Light hydrocarbon liquids and two-phase streams are included in the "Light Liquid/Two-Phase" group. The "Heavy Liquids" group contains those streams which consist primarily of kerosene and heavier hydrocarbon liquids. Compressor seal emissions do not vary according to these three process streams, instead the emissions are broken down by a) hydrocarbon service and b) hydrogen service. The stream group is determined by the most volatile stream component present in a concentration of 20% or more.

The approximate numbers of each type of source selected for study and testing in each refinery were:

valves	250-300
flanges	100-750
pump seals	100-125
compressor seals	10- 20
drains	20- 40
relief valves	20- 40

There were normally 500-600 sources studied in each refinery.

The distribution of sources among the process units was determined before the selection and testing of individual sources was begun. Individual sources were selected from piping, instrumentation and process flow diagrams before a refinery processing area was entered. Only those preselected sources were screened. In this way, bias based on observation of individual sources was eliminated, and an approximate random sample set within the required source distribution was achieved.

The screening of sources was accomplished with sensitive portable hydrocarbon detectors. The principal device used in this study was the J. W. Bacharach Instrument Co. "TLV Sniffer". The Century Instrument Co. Organic Vapor Analyzer (Model OVA-108) was used for some screening, but these values were not included in the correlation calculations which follow. The instruments were calibrated with standard mixtures of hexane in air. The OVA-108 and TLV Sniffer give direct readings of hydrocarbon concentrations in ppm by volume. In this report, the terms "screening values" and "TLV screening values" refer to the maximum hydrocarbon concentration detected at selected baggable sources.

TABLE 3-3. PROCESS STREAM CLASSIFICATION BY GROUP

<u>STREAM GROUP¹</u>	<u>HYDROCARBON STREAM DESCRIPTION²</u>
Gas/Vapor	C ₁ -C ₂ Hydrocarbons C ₃ -C ₄ Hydrocarbons C ₅ -C ₉ Hydrocarbons C ₁₀ + Hydrocarbons Mixed Molecular Weight Hydrocarbon Streams Aromatic Hydrocarbons Miscellaneous Organic Compounds Hydrocarbon Streams Containing H ₂ , H ₂ S, and H ₂ O
Light Liquids/Two-Phase	C ₂ Hydrocarbons C ₃ -C ₄ Hydrocarbons C ₅ -C ₆ Hydrocarbons C ₇ -C ₉ Hydrocarbons Naphtha Light Distillate Aromatic Hydrocarbons (low molecular weight) Miscellaneous Streams
Heavy Liquids	Kerosene, Diesel, Heating Oil Gas Oils Atmospheric Resid/Vacuum Gas Oil Vacuum Resid/Asphalt Aromatics/Polymers Mixed Molecular Weight Streams Non-distillate Solvents Miscellaneous Organic Streams

¹Stream group is determined by the stream conditions within the process lines

²The most volatile stream component present at a concentration of 20% or more determines the stream classification.

When screening valves, pumps or compressors, the probe of the hydrocarbon detector was normally placed as close as possible to the intersection of the shaft with the sealing device (0 cm). The probe was held at this location for a minimum of five seconds. The detector reading was recorded. This was repeated at three other points 90° apart around the shaft. The maximum reading was used as the sampling criterion.

Flanges were screened by placing the detector probe at 2-inch intervals all around and right against the outside perimeter of the flange interface. The maximum detector reading was recorded. Drains were similarly screened. The detector probe was placed at 2-inch intervals around the perimeter of the drain. The maximum measured hydrocarbon concentration was recorded.

Relief valves were screened by placing the instrument probe at the valve "horn" exit. The screening value obtained at that point was used as the sampling criterion.

The values of all choice variables and correlating parameters were recorded at the time of screening. The leak rates from sources with screening values below 200 ppmv hydrocarbon were considered to be negligible. All sources with screening values of 200 ppmv or greater were candidate sources for sampling to measure their leak rates. Time and equipment constraints prevented all candidate sources from being sampled; emissions from the candidate sources which were not sampled were estimated as described in Appendix A. At the time of sampling, all sources were rescreened. Values of the recorded source data were checked and, if necessary, changed to conform to the conditions existing at the time of sampling.

SECTION 4

RESULTS OF SCREENING AND SAMPLING PROGRAM

The results of this program are summarized in this section of the report. The screening results are described and interpreted. The frequency of leaks from the various baggable sources are presented. The emission factors which were developed from the sampling results are given.

Relationships Between Screening Readings and Nonmethane Leak Rates

One of the important results of this study has been the establishment of relationships between concentrations obtained using portable hydrocarbon detection devices and measured leak rates. The use of these portable devices to estimate leak rates has potential for refinery maintenance programs, as well as in determining total leak rates for regulatory purposes. The data analyzed in this section were obtained primarily using a J.W. Bacharach "TLV Sniffer" calibrated to hexane (by volume). Another portable device, the Century Instrument Company's Organic Vapor Analyzer (Model OVA-108), was also used and evaluated. The OVA-108 screening values were found to have similar, but not identical, correlations with leak rates. Most readings were obtained by placing the detector probe directly on the sources. However, for evaluation purposes, some readings were also obtained five centimeters from the source. It is possible to relate the various kinds of screening values to one another. For this report, however, the correlations are based on "TLV Sniffer" readings at the source.

Screening values were obtained when the source was first located, and rescreening values were taken at the time each source was sampled. The rescreening values are generally more highly correlated with leak rates than are the original screening results. For example, the correlation coefficient for the correlation of maximum screening (original) values with nonmethane hydrocarbon leak rates of valves is 0.63. A correlation coefficient of 0.72 is obtained when the maximum rescreening values are correlated with non-methane hydrocarbon leak rates of valves.

Appendix A contains detailed descriptions of the statistical procedures used to develop the results presented in this report. The least-square linear regression equations developed for predicting leak rates from unsampled sources in the data base are described. For potential prediction purposes outside this data base, a statistical analysis of covariance was done to determine whether different linear equations are required for each baggable source and stream type. The results of this analysis are presented in Appendix A. It was found that the source and stream types could be grouped such that three equations were adequate for predicting leak rates from screened sources. The three groups are as follows:

- Valves and Flanges - Gas/Vapor Streams
- Valves and Flanges - Light Liquid/Two-phase and Heavy Liquid Streams
- Pump Seals, Compressor Seals, Drains, Relief Valves

The equations were used to develop nomographs which relate the predicted leak rate and maximum screening values for the various source and stream types. These nomographs are presented in Figures 4-1 through 4-6.

Each nomograph gives the predicted mean leak rate for different values of maximum TLV screening readings taken directly on the source of the leak. Ninety percent confidence intervals for the true mean leak rate are also given. These confidence limits are for the mean leak rate and should not be confused with confidence intervals for individual leak rates for given screening values. Table 4-1 compares the 90% confidence intervals for the mean leak rate and the 90% confidence intervals for individual leaks for selected screening values.

Emission Factors and Frequency of Leaks

The estimated emission factors for nonmethane hydrocarbon emissions from six types of sources are summarized in Table 4-2. Overall emission factors, as well as factors for sources in different process stream services, are included. The process stream breakdown for flanges, drains and relief valves are included for information purposes. Summary statistics are tabulated for each source type. These include (1) 95% confidence intervals for both the emission factors and for percent of leaking sources, (2) percentile for individual leaks, and (3) emission factor percentile. The 95% confidence interval is the interval or range of values expected to include the true emission factor or true percent of leaking sources, with 95% confidence. For example, the true emission factor for relief valves (if all relief valves could be sampled and averaged) should be between 0.06 and 0.52 lb/hr.

If a random selection of sources are sampled and ranked according to their emission rates, the range of emission rates excluding the first 1% and last 1% of the sampled sources is the expected range of leak rates (1st and 99th). As an example, the 1% of relief valves with the lowest emission rates would emit nothing. The 1% of relief valves with the highest emission rates are expected to emit more than 4.9 lb/hr from each valve. Therefore, 98% of all relief valves would be expected to have leak rates between zero and 4.9 lb/hr.

The population percentile for emission factors represents the leak rate percentile at which the emission factor is expected to be located in a random sample of a particular source type. For instance, the percentile for relief valves is 91.9 which means that one could expect about 92% of the leak rates from relief valves to be less than the emission factor of 0.19 lb/hr. About 8% of the relief valve leaks could be expected to be greater than the emission factor. The fact that most of the emission factor percentiles are

(Part I: Screening Values from 0-10,000 ppm)

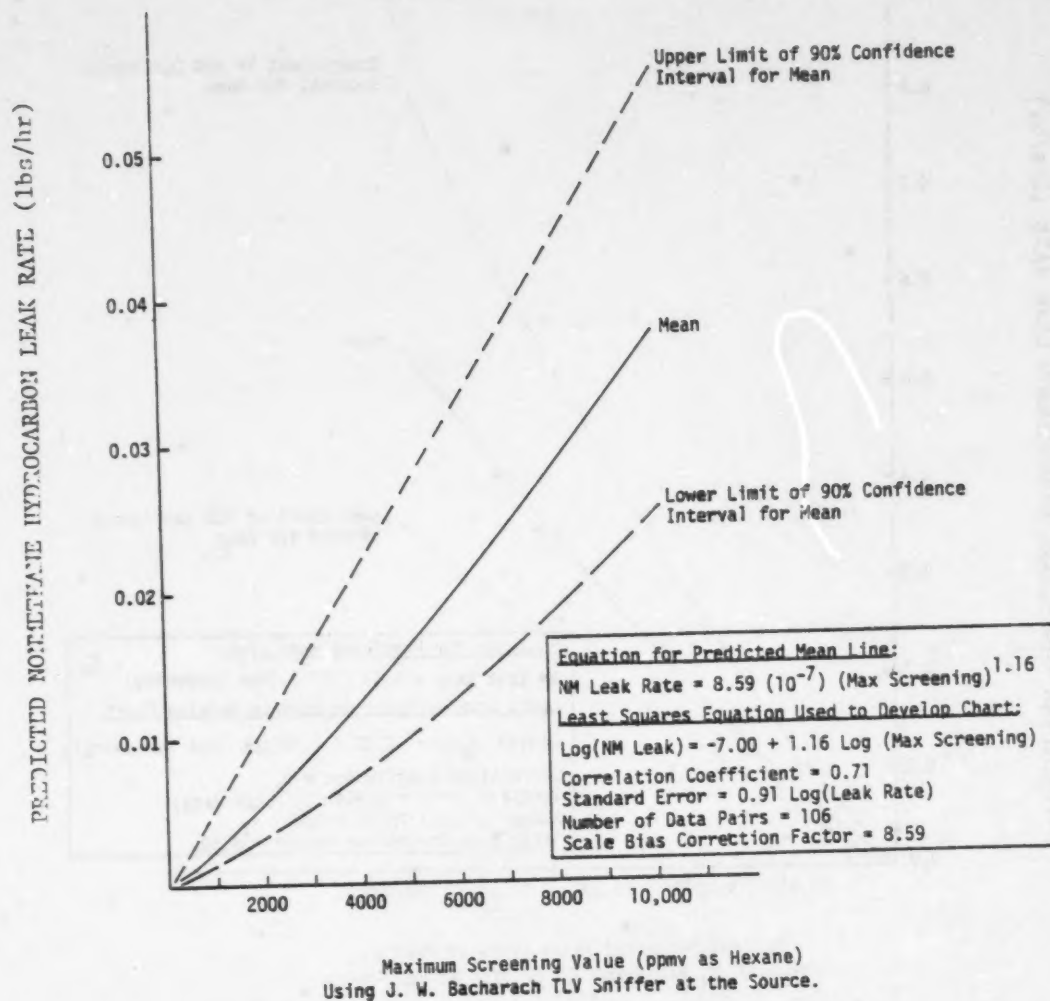


Figure 4-1. Valves and Flanges - Gas/Vapor Streams - Part I
 Nomograph for Predicting Total Nonmethane Hydrocarbon
 Leak Rates from Maximum Screening Values

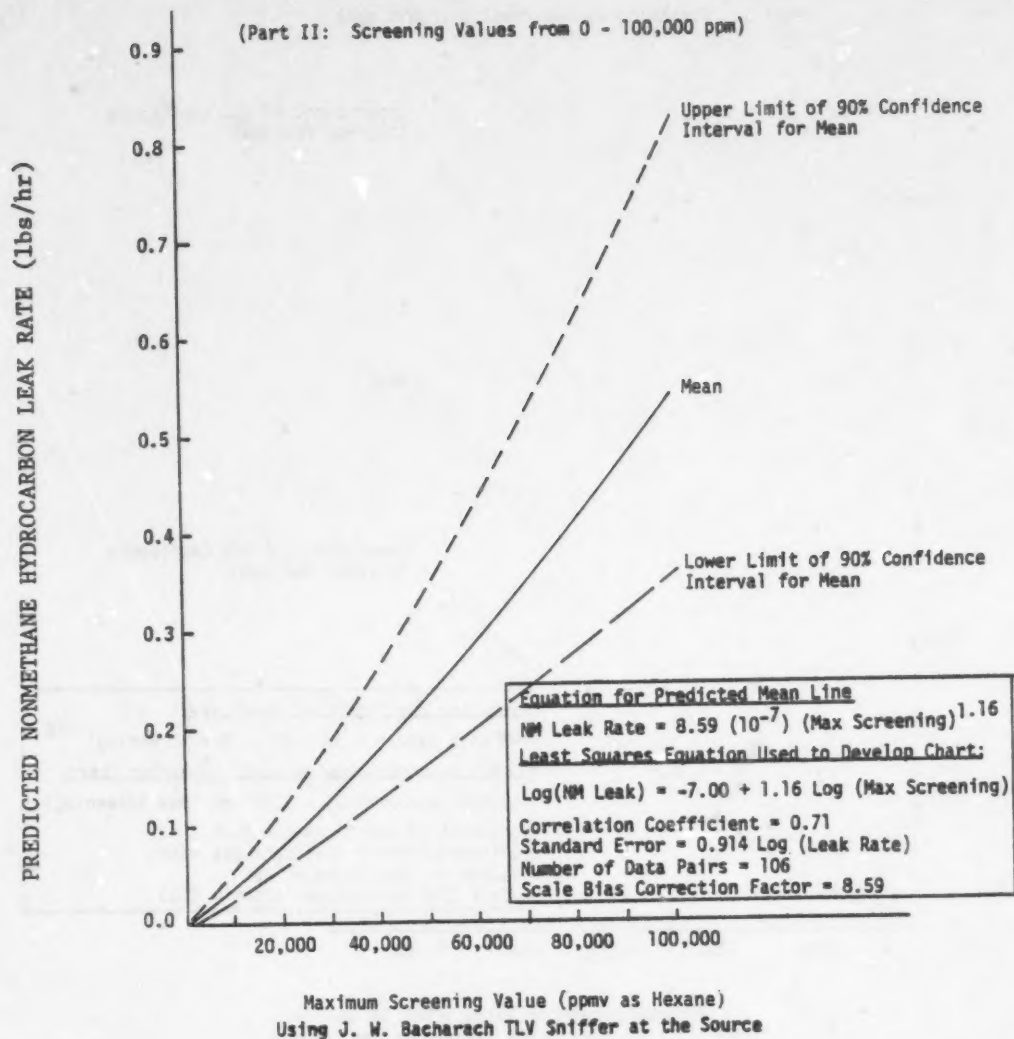


Figure 4-2. Valves and Flanges - Gas/Vapor Streams - Part II
 Nomograph for Predicting Total Nonmethane Hydrocarbon
 Leak Rates from Maximum Screening Values

(Part I: Screening Values from 0-10,000 ppm)

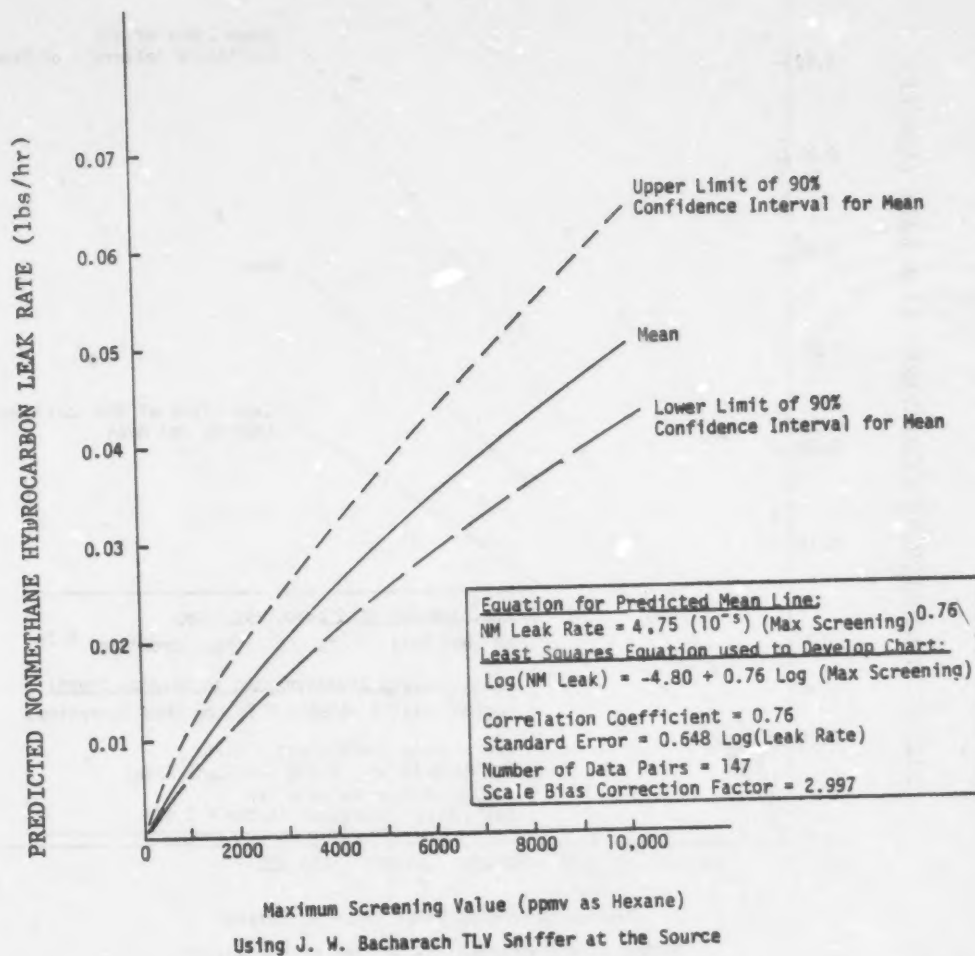


Figure 4-3. Valves and Flanges - Light Liquid/Two-Phase and Heavy Liquid Streams - Part I

Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values

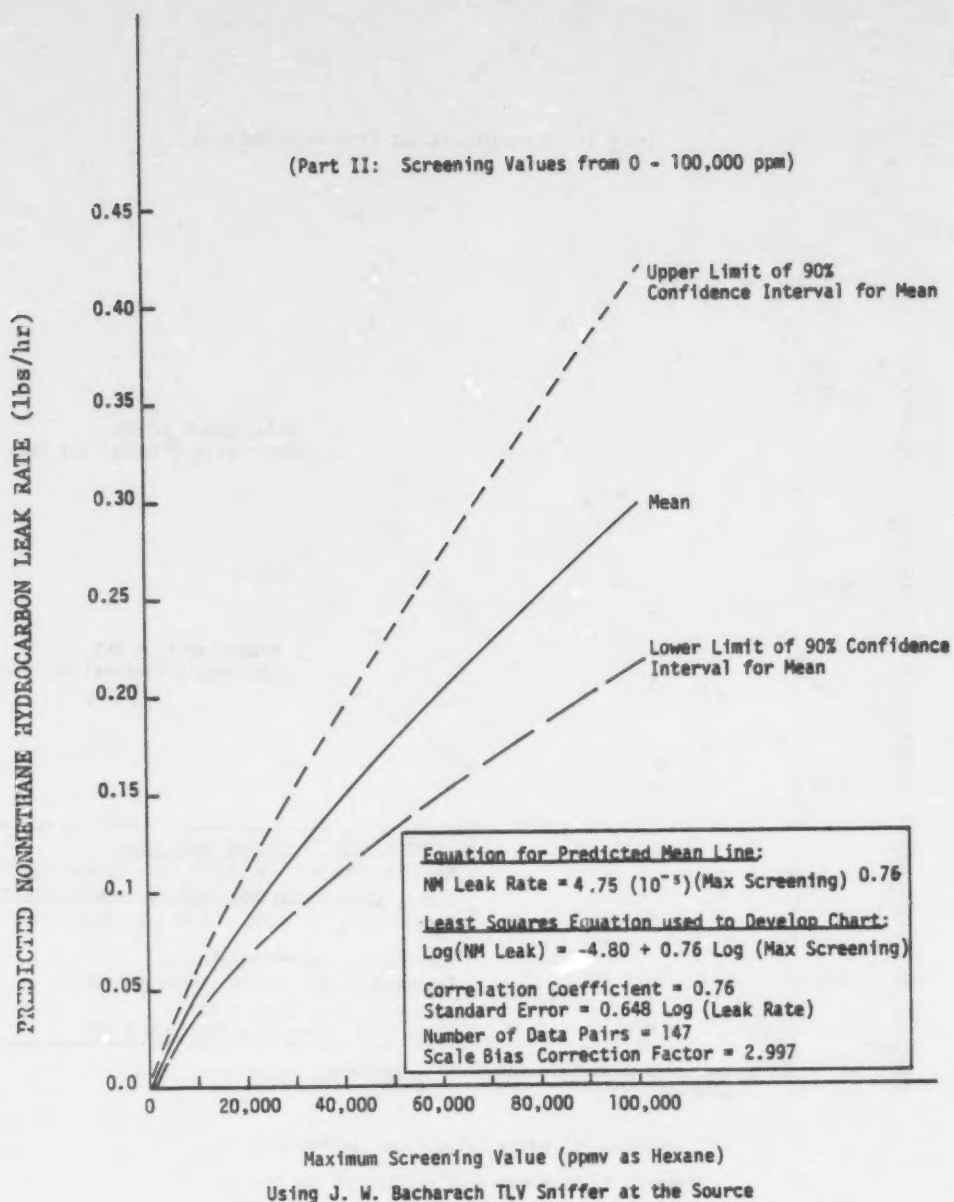


Figure 4-4. Valves and Flanges - Light Liquid/Two-Phase and Heavy Liquid Streams - Part II

Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values

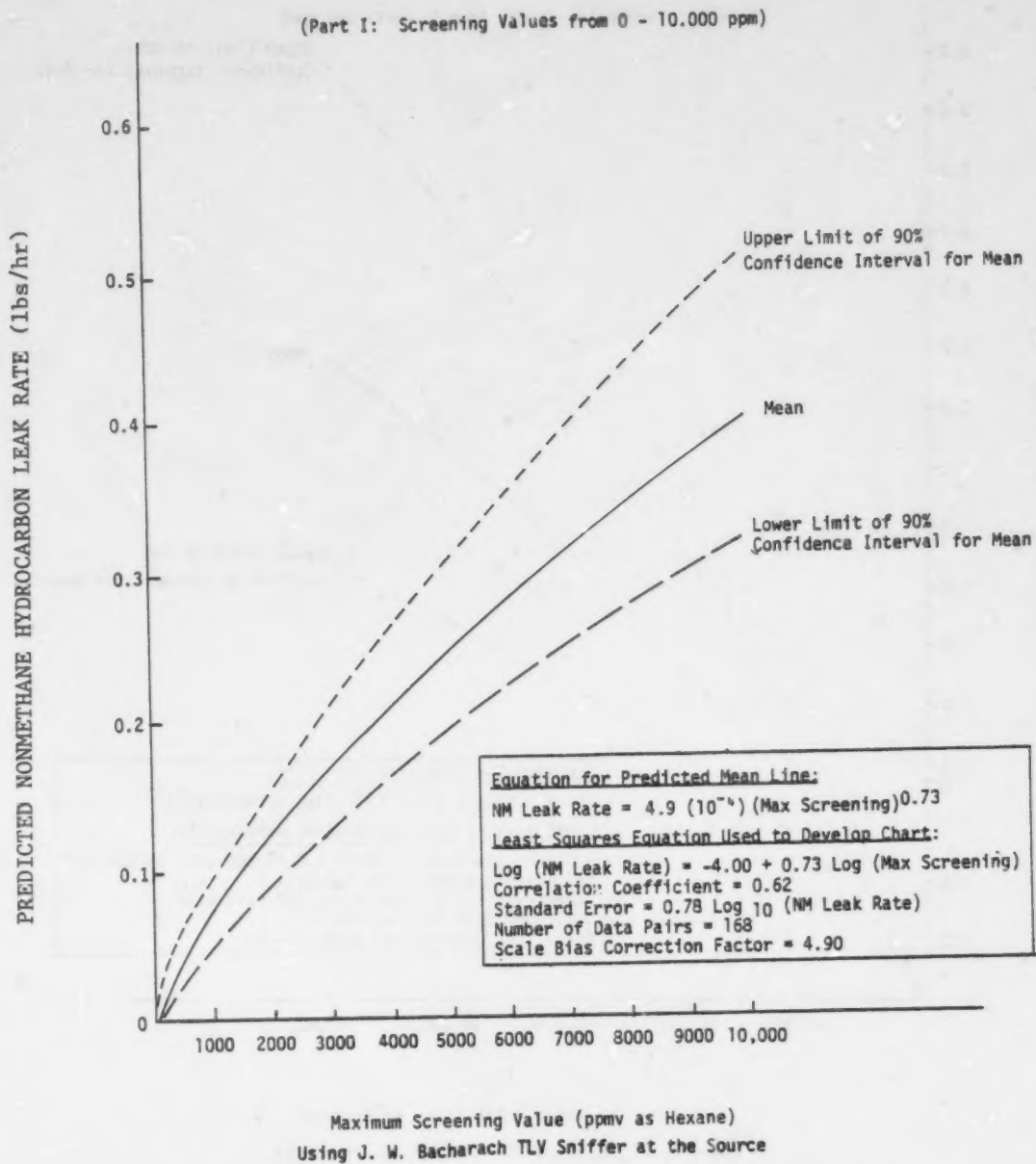


Figure 4-5. Pumps, Compressors, Drains, Relief Valves - Part I
 Nomograph for Predicting Total Nonmethane Hydrocarbons
 Leak Rates from Maximum Screening Values

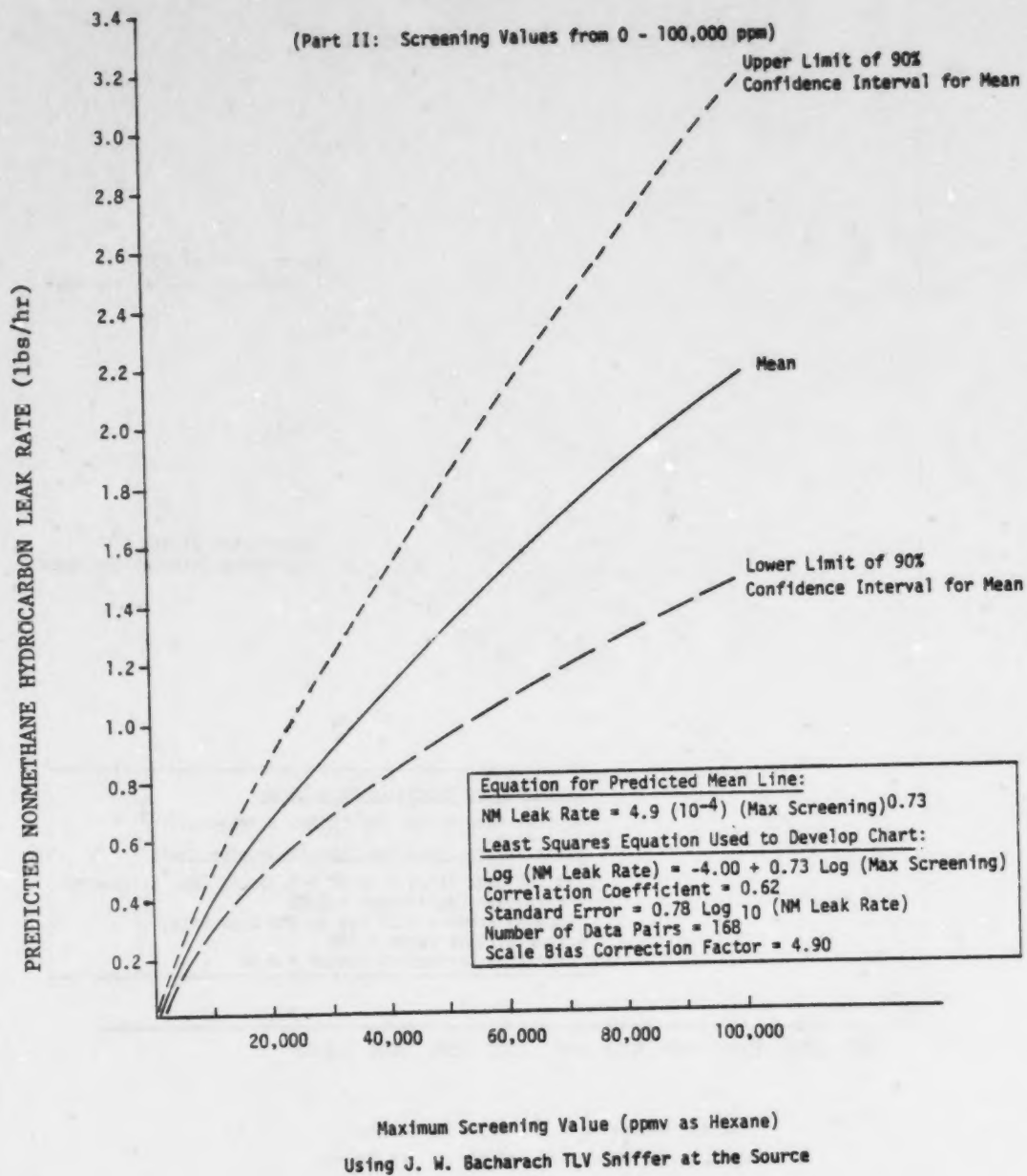


Figure 4-6. Pumps, Compressors, Drains, Relief Valves - Part II

Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values

TABLE 4-1. CONFIDENCE INTERVALS FOR MEAN AND INDIVIDUAL LEAK RATES
VALVES AND FLANGES - GAS/VAPOR STREAMS

MAXIMUM SCREENING VALUE (ppmv)	PREDICTED MEAN LEAK RATE (lbs/hr)	90% CONFIDENCE INTERVAL FOR:	
		MEAN LEAK (lbs/hr)	INDIVIDUAL LEAKS (lbs/hr)
1	10^{-7}	(0.000 , 10^{-6})	(0.000 , 10^{-4})
200	10^{-5}	(0.000 , 0.001)	(0.000 , 0.02)
500	0.001	(0.000 , 0.003)	(0.000 , 0.04)
1,000	0.003	(0.001 , 0.005)	(0.000 , 0.09)
3,000	0.009	(0.005 , 0.02)	(0.000 , 0.31)
5,000	0.017	(0.01 , 0.03)	(0.001 , 0.56)
10,000	0.038	(0.02 , 0.06)	(0.001 , 1.2)
20,000	0.084	(0.06 , 0.12)	(0.003 , 2.7)
50,000	0.24	(0.17 , 0.35)	(0.007 , 7.9)
100,000	0.54	(0.36 , 0.82)	(0.02 , 17.7)

(Cont'd.) TABLE 4-1. CONFIDENCE INTERVALS FOR MEAN AND INDIVIDUAL LEAK RATES
VALVES AND FLANGES - LIGHT LIQUID/TWO-PHASE
AND HEAVY LIQUID STREAMS

MAXIMUM SCREENING VALUE (ppmv)	PREDICTED MEAN LEAK RATE (lbs/hr)	90% CONFIDENCE INTERVAL FOR:	
		MEAN LEAK (lbs/hr)	INDIVIDUAL LEAKS (lbs/hr)
1	5×10^{-5}	(0.000 , 10^{-6})	(0.000 , 0.001)
200	0.003	(0.001 , 0.004)	(0.000 , 0.03)
500	0.005	(0.004 , 0.007)	(0.000 , 0.06)
1,000	0.009	(0.007 , 0.01)	(0.001 , 0.11)
3,000	0.021	(0.02 , 0.03)	(0.002 , 0.24)
5,000	0.031	(0.02 , 0.04)	(0.003 , 0.36)
10,000	0.052	(0.04 , 0.06)	(0.004 , 0.61)
20,000	0.088	(0.07 , 0.11)	(0.007 , 1.0)
50,000	0.18	(0.13 , 0.24)	(0.01 , 2.1)
100,000	0.30	(0.22 , 0.42)	(0.02 , 3.6)

(Cont'd.) TABLE 4-1. CONFIDENCE INTERVALS FOR MEAN AND INDIVIDUAL LEAK RATES
PUMP SEALS, COMPRESSOR SEALS, DRAINS, RELIEF
VALVES - ALL PROCESS STREAM TYPES

MAXIMUM SCREENING VALUE (ppmv)	PREDICTED MEAN LEAK RATE (lbs/hr)	90% CONFIDENCE INTERVAL FOR:	
		MEAN LEAK (lbs/hr)	INDIVIDUAL LEAKS (lbs/hr)
1	0.0005	(0.000 , 0.002)	(0.000 , 0.01)
200	0.023	(0.01 , 0.04)	(0.001 , 0.47)
500	0.046	(0.03 , 0.07)	(0.002 , 0.90)
1,000	0.076	(0.06 , 0.10)	(0.003 , 1.5)
3,000	0.17	(0.13 , 0.22)	(0.009 , 3.3)
5,000	0.25	(0.20 , 0.31)	(0.01 , 4.8)
10,000	0.41	(0.32 , 0.51)	(0.02 , 7.9)
20,000	0.68	(0.52 , 0.88)	(0.03 , 13.)
50,000	1.3	(0.96 , 1.8)	(0.07 , 26.)
100,000	2.2	(1.5 , 3.2)	(0.12 , 43.)

TABLE 4-2. SUMMARY STATISTICS AND ESTIMATED VAPOR EMISSION FACTORS
FOR NONMETHANE HYDROCARBONS FROM BAGGABLE SOURCES

SOURCE TYPE	TOTAL SCREENED ¹	NUMBER LEAKING ²	PERCENT LEAKING	95% CONFIDENCE INTERVAL FOR PERCENT LEAKING	PERCENTILE FOR INDIVIDUAL LEAKS (lb/hr) 1st 99th	EMISSION FACTOR ESTIMATE (lb/hr-source)	95% CONFIDENCE INTERVAL FOR EMISSION FACTOR (lb/hr-source)	EMISSION FACTOR PERCENTILE
VALVES								
Gas/Vapor Streams	683	200	29.3	(25.9, 32.7)	0	0.61	(0.027, 0.084)	94.4
Light Liquid/Two-Phase Streams	1019	372	36.5	(33.6, 39.5)	0	0.31	(0.016, 0.034)	89.7
Heavy Liquid Streams	522	35	6.7	(4.6, 8.9)	0	0.08	(0.0002, 0.002)	95.8
PUMP SEALS								
Light Liquid Streams	470	300	63.8	(58.9, 68.8)	0	4.0	(0.17, 0.39)	89.8
Heavy Liquid Streams	292	66	22.6	(17.1, 28.1)	0	0.87	(0.02, 0.11)	88.4
FLANGES (ALL)								
Gas/Vapor Streams	2030	62	3.1	(2.2, 3.9)	0	0.008	(0.0002, 0.001)	97.4
Light Liquid/Two-Phase Streams	369	10	2.7	(0.8, 4.6)	0	0.008	(10 ⁻³ , 0.005)	
Heavy Liquid Streams	616	33	5.4	(3.3, 7.4)	0	0.011	(0.0002, 0.001)	
	325	6	1.9	(0.2, 3.5)	0	0.009	(10 ⁻³ , 0.02)	
COMPRESSOR SEALS								
Hydrocarbon Service	145	102	70.3	(62.9, 77.7)	0	17.0	(0.46, 2.0)	83.4
Hydrogen Service	85	69	81.2	(71.2, 88.8)	0	2.0	(0.04, 0.24)	86.5
DRAINS (ALL)								
Light Liquid/Two Phase Streams	255	49	19.2	(14.4, 24.0)	0	1.3	(0.02, 0.20)	93.3
Heavy Liquid Streams	100	26	26.0	(14.6, 37.4)	0	1.9	(0.02, 0.32)	
	107	19	17.8	(9.5, 26.1)	0	0.63	(0.003, 0.21)	
RELIEF VALVES (ALL)								
Gas/Vapor Streams	148	58	39.2	(25.1, 40.6)	0	4.9	(0.06, 0.52)	91.9
Light Liquid/Two Phase Streams	92	42	45.6	(35.2, 56.4)	0	4.0	(0.10, 1.30)	
Heavy Liquid Streams	28	7	25.0	(10.7, 44.9)	0	0.38	(0.001, 0.23)	
	23	8	34.8	(16.4, 57.3)	0	0.42	(0.001, 0.20)	

¹Some streams could not be accurately classified into stream category so the totals are not the sum of the stream groups.

²Leaking sources in this report are defined as sources with screening values greater than or equal to 200 ppmv or sources with measured leaks greater than 0.00001 lb/hr.

greater than 90% is an indication of the extreme skewness of the leak rate data.

A very high degree of correlation was found between mass emission rates and the type of stream service in which the sources were employed. The process stream groups are described in Table 3-3 of this report.

It is evident from Table 4-2 that individual sources in gas/vapor stream service emit more hydrocarbons than comparable sources in heavy liquid service. On the average, for example, valves in gas/vapor service emit more than 70 times as much material as valves in heavy liquid service.

Because of the large influence of stream type on source emissions, overall emission factors for valves and pump seals are not presented. Due to the experimental design, the distribution of sampled valves and pump seals among the stream groups is not representative of the overall distribution of sources within refineries. Thus, overall emission factors for valves and pump seals, as determined from the sampling program, are not directly applicable to either entire refineries or individual process units. The stream group distributions must be known or estimated to develop accurate overall process unit and refinery emission factors for these two source types.

The emission factors for valves given in Table 4-2 were developed for in-line pipeline valves. The emission points were around the valve stem and around the perimeter of the packing gland. A small number of open-ended valves were also sampled, such as drain valves and sampling valves. The screening and sampling point for these valves was the open-end of the pipe downstream from the valve. The emission occurred through the valve seat rather than around the valve stem. The average emission factor for these open-ended valves was 0.007 lb/hr with a 95% confidence interval of 0.002 - 0.016 lb/hr. A total of 129 open-ended valves were screened, and 30 were found to have screening values $\geq$ 200 ppmv hydrocarbon.

Distribution of Sources within a Refinery

In order to ascertain the relative contribution of the various source types, the number of sources of each type and stream classification in a refinery must be known. Some counting of source types was done during this sampling program, but these counts were not recorded by process stream groups. To give an indication of the relative importance of the various source types, a hypothetical refinery model has been used. The model is based on the ADL-Texas Gulf Cluster Model¹ processing 330,000 BPCD of crude. The total number of fittings in the various process units in this hypothetical model are estimated from counts of fittings made during this program.

Since very little information is available on the number of sources in the various types of stream service, two cases are presented:

¹Kittrell, J.R., Impact of SOX Emissions Control on Petroleum Refining Industry, Volume II. Detailed Study Results, EPA/699/2-76/161B, June 1976

Case I - The distribution of stream types for valves is weighted toward liquid streams, the distribution for pump seals is weighted toward the heavy liquid streams, and the distribution for compressor seals is weighted toward hydrogen service.

Case II - The distribution of stream types for valves is weighted toward gas service, the distribution for pump seals is weighted toward light liquid streams, and the distribution of compressor seals is weighted toward hydrocarbon service.

It should be emphasized that these two cases and the hypothetical refinery model are being used only for exemplary purposes in this report. An equivalent analysis can be done for any particular situation using appropriate number of sources and stream classifications in conjunction with the emission factors in this report.

Table 4-3 shows the number of sources for the above two cases in the hypothetical refinery and the results of applying the emission factors from Table 4-2 to these numbers. The emissions thus obtained have been divided by the total emissions from all source types to give the percent of total non-methane hydrocarbon emissions attributable to each source category.

For this hypothetical refinery model, it is clear that valves, because of their number and relatively high emission factors, are the major emission source among the source categories included in this report. Depending on the case, valves are expected to contribute from 61 to 67 percent of the total emissions from the six source types in this hypothetical refinery.

Although flanges represent the greatest number of any source type in the hypothetical model, their small emission factor results in an expected contribution of only 6 to 8 percent of total emissions. The contribution from drains has an expected value of 11 to 15 percent. Pump seals, compressor seals, and relief valves each have maximum expected contributions of 9 percent or less, using this model.

Distribution of Leak Rates

Table 4-4 gives the distribution of measured and estimated nonmethane hydrocarbon emission rates for each source type. It is obvious from this table that the bulk of the emissions emanate from a small percentage of the sampled fittings. The table represents an idealized situation for reducing emissions by selective maintenance of sources. For example, the table indicates that if a particular 3.6% of the valves in gas/vapor service in a refinery (those with leak rates greater than 0.1 lbs/hr) could be repaired such that the leak rate of each such valve was reduced to zero, then 91.1% of the mass emissions attributable to valves in gas/vapor service could be eliminated. The problem in practical implementations of such a repair program is locating those particular 3.6% of the valves in gas/vapor service with leak rates greater than 0.1 lbs/hr without bagging and sampling all such valves in a refinery.

TABLE 4-3. HYPOTHETICAL REFINERY - BASED ON ADL TEXAS
GULF CLUSTER MODEL (330,000 BPCD)

SOURCE TYPE	NUMBER OF SOURCES (PERCENT)		PERCENT OF TOTAL NONMETHANE HYDROCARBON EMISSIONS	
	CASE I	CASE II	CASE I	
			ESTIMATE (95% CI) ¹	ESTIMATE (95% CI) ²
Valves	14300	14300	61.6	67.3
Gas/Vapor	1430 (10%)	4290 (30%)	17.6 (10.1, 31.4)	40.4 (23.2, 72.1)
Light Liquid	7150 (50%)	5720 (40%)	43.0 (29.9, 63.5)	26.3 (18.3, 38.9)
Heavy Liquid	5720 (40%)	4290 (30%)	1.0 (0.3, 3.0)	0.6 (0.2, 1.7)
Pump Seals	264		9.1 (6.3, 13.6)	9.2 (6.3, 13.5)
Light Liquid	106 (40%)	158 (60%)	7.2 (4.7, 10.8)	8.2 (5.4, 12.3)
Heavy Liquid	158 (60%)	106 (40%)	1.9 (0.8, 4.5)	1.0 (0.4, 2.3)
Compressor Seals	27	27	3.9 (2.0, 7.7)	4.1 (1.9, 8.1)
Hydrocarbon Service	14 (52%)	20 (74%)	3.6 (1.7, 7.3)	3.9 (1.8, 8.0)
Hydrogen Service	13 (48%)	7 (26%)	0.3 (0.1, 0.8)	0.2 (0.01, 0.15)
Flanges	51200	51200	7.7 (2.9, 13.4)	5.9 (2.2, 10.2)
Drains	793	793	14.5 (4.1, 41.4)	11.1 (3.2, 31.7)
Relief Valves (venting to atmosphere)	64	64	3.2 (1.0, 3.9)	2.4 (0.8, 6.7)
			100%	100%

¹ Case I - distribution of stream types for valves and pump seals is weighted toward heavier streams.

² Case II - distribution of stream types for valves and pump seals is weighted toward lighter streams.

³ 95% CI - 95% confidence interval for percent of emissions from process fittings attributable to a particular source type. The width of the interval is due only to the uncertainty in emission factors; the percentage of each source type is assumed fixed or known.

⁴ Total is the sum of nonmethane hydrocarbon emissions from the six source types discussed in this table.

TABLE 4-4. DISTRIBUTION OF MEASURED LEAK RATES¹

Leak Range (lb/hr)	VALVES									
	PUMP SEALS					RELIEF VALVES				
	Gas/Vapor Streams	Light Liquid/ Two-Phase Streams	Heavy Liquid Streams	Light Liquid Streams	Heavy Liquid Streams	Drains	Flanges	Compressor Seals	Hydrogen Service	Hydrocarbon Service
>1.0	A 1.0	A 0.0	A 0	A 4.0	A 90.5	A 1.5	A 0	A 15.9	A 33.1	A 16.6
0.1-1.0	B 68.4	B 13.8	B 0.2	B 15.7	B 24.8	B 63.2	B 0.0	B 74.2	B 24.3	B 1.4
0.01-0.1	A 2.6	A 3.3	A 0.9	A 22.5	A 4.3	A 30.1	A 63.2	A 16.5	A 25.9	A 0.1
0.001-0.01	B 22.7	B 58.8	B 2.7	B 16.4	B 0.4	B 6.0	B 0.0	B 1.4	B 24.7	B 0.0
0.00001-0.001	A 8.9	A 3.5	A 2.9	A 4.9	A 0.0	A 0.7	A 0.1	A 14.1	A 14.1	A 0.0
>0.00001	B 8.1	B 0.2	B 6.7	B 63.5	B 22.6	B 100%	B 100%	B 81.2	B 81.2	B 100%
	29.2%	36.3%	6.7%	63.5%	22.6%	100%	100%	81.2%	81.2%	100%

A - Percent of total sources screened with sampled leak rates within leak range.

B - Percent of total mass emissions attributable to sources within leak range.

1 - Most sources were bagged and sampled to obtain leak rates; some were estimated using procedures described in Section 1 of Appendix A.

This is obviously impractical, so the identification of sources requiring maintenance must occur through some type of screening program.

Distribution of Emissions and Sources Based on Screening Values

A convenient tool both for monitoring hydrocarbon emission sources and estimating source leak rates is the portable hydrocarbon detector. From the results of this study, nomographs have been prepared relating hydrocarbon concentration at the source (screening value) to the percentage of each source type expected to have screening values above any selected value. Other nomographs have been prepared relating screening values to the percentage of total mass emissions which can be expected from sources with screening values greater than any given value. (See Appendix A for a discussion of nomograph development.)

These nomographs for the six source types (and stream groups for valves, compressors, and pump seals) are presented in Figures 4-7 through 4-16. The "A" figures relate the percent of total mass emissions for a given source category to screening values; the "B" figures relate the percent of sources to screening values. The screening values in these nomographs are the hydrocarbon concentrations obtained at the source (zero cm) with a Bacharach TLV Sniffer calibrated with hexane.

Confidence intervals are included on each of these nomographs. The statistical procedures used to develop these intervals are discussed in section 4.2 and 4.3 of Appendix A. The confidence intervals for both types of nomographs indicate how well the cumulative function has been estimated from the data collected in this program.

The 95 percent confidence intervals for the cumulative percent of sources can be interpreted as ranges of values which contain the actual percent from the population of sources studied. Note that these intervals apply to the entire population of sources (i.e., a composite of all United States refineries), and are not necessarily applicable to a finite number of sources at any particular refinery. Because of the nature of the function, the confidence intervals will be approximately valid anytime a random sample of greater than 100 sources is being considered.

The 90% confidence intervals for the cumulative percent of total emissions function can be interpreted as ranges of values which contain the actual percent of total emissions function for the entire population of sources. Again, these intervals describe how well the function has been estimated for the entire population and are not directly applicable to a particular refinery situation with a finite number of sources. The variation of the function for a particular sample of sources is a complex function of the number of sources. Section 4-3 of Appendix A discusses this issue further and gives an example of particular confidence bounds for valves in light liquid/two-phase service.

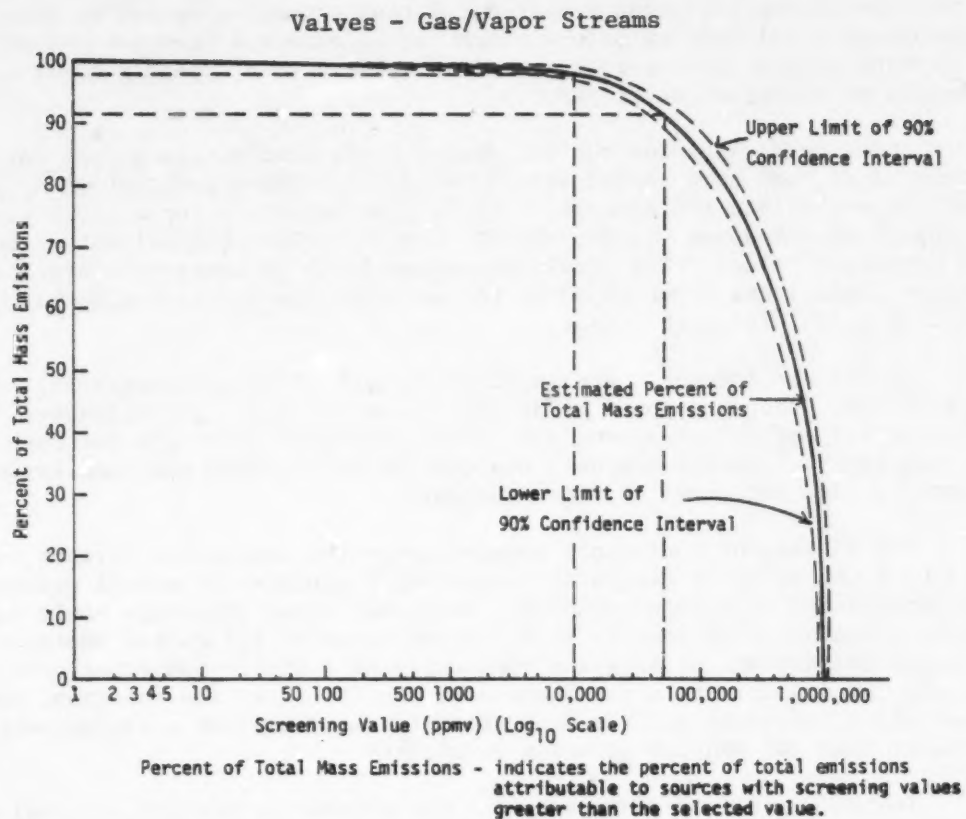
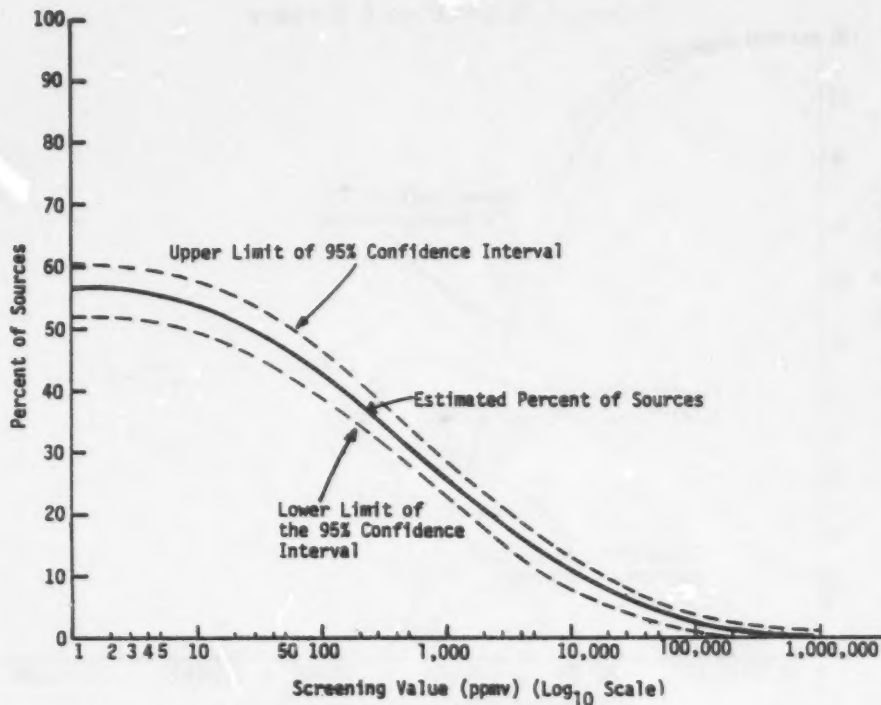


Figure 4-7A. Cumulative Distribution of Total Emissions by Screening Values - Valves - Gas/Vapor Streams

Valves - Light Liquid/Two-Phase Streams



Percent of Sources - Indicates the percent of sources with screening values greater than the selected value.

Figure 4-8B. Cumulative Distribution of Sources by Screening Values - Valves - Light Liquid/Two-Phase Streams

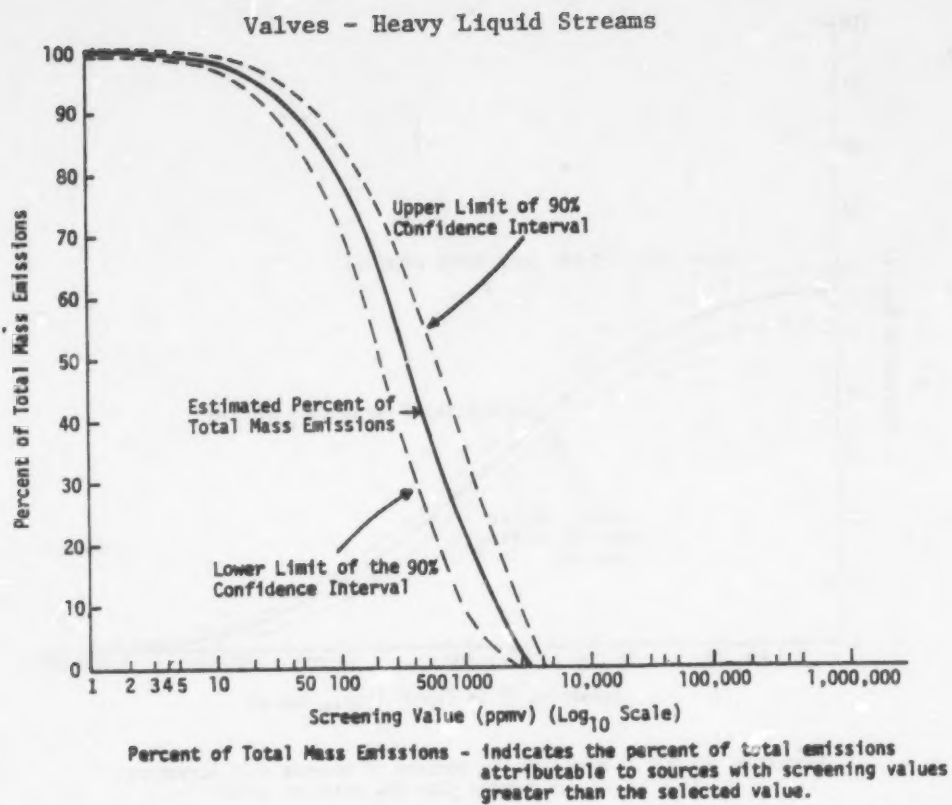
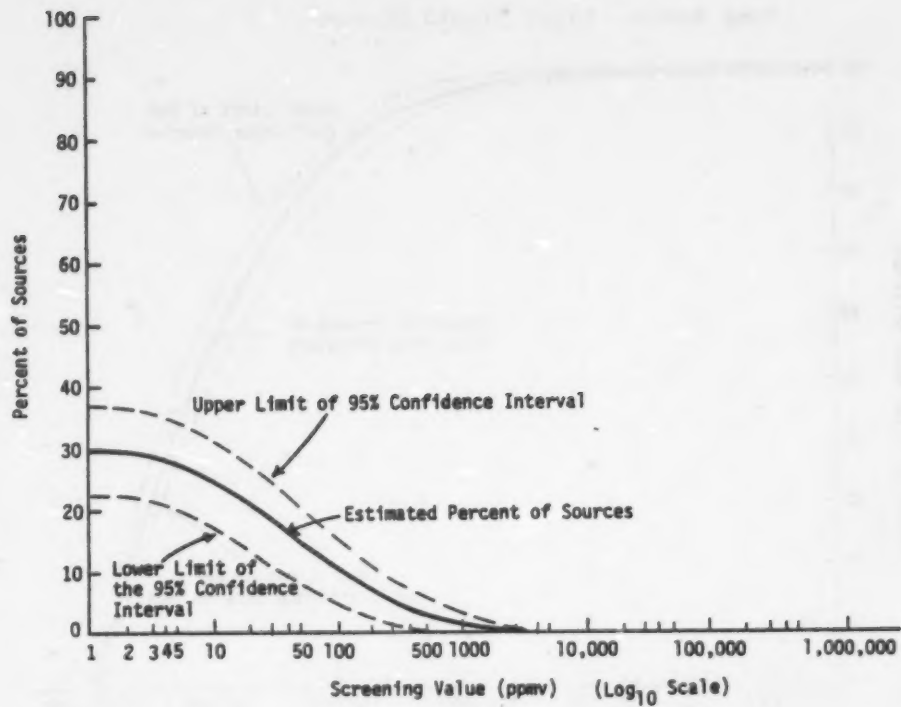


Figure 4-9A. Cumulative Distribution of Total Emissions by Screening Values - Valves - Heavy Liquid Streams

Valves - Heavy Liquid Streams



Percent of Sources - indicates the percent of sources with screening values greater than the selected source.

Figure 4-9B. Cumulative Distribution of Sources by Screening Values - Valves - Heavy Liquid Streams

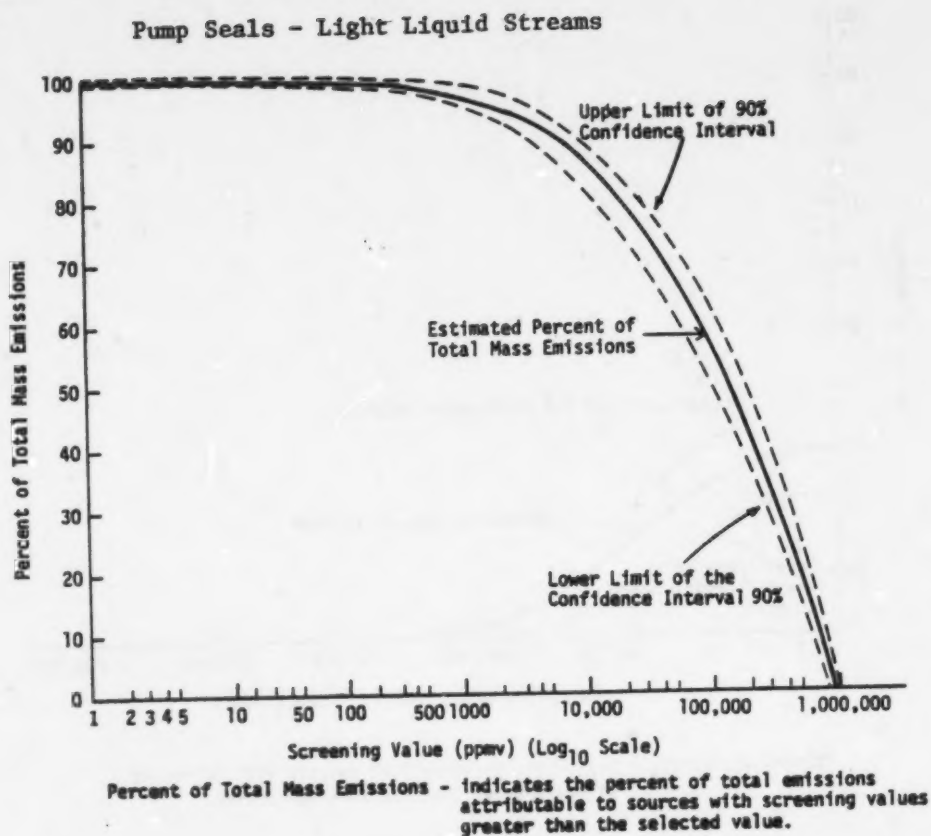
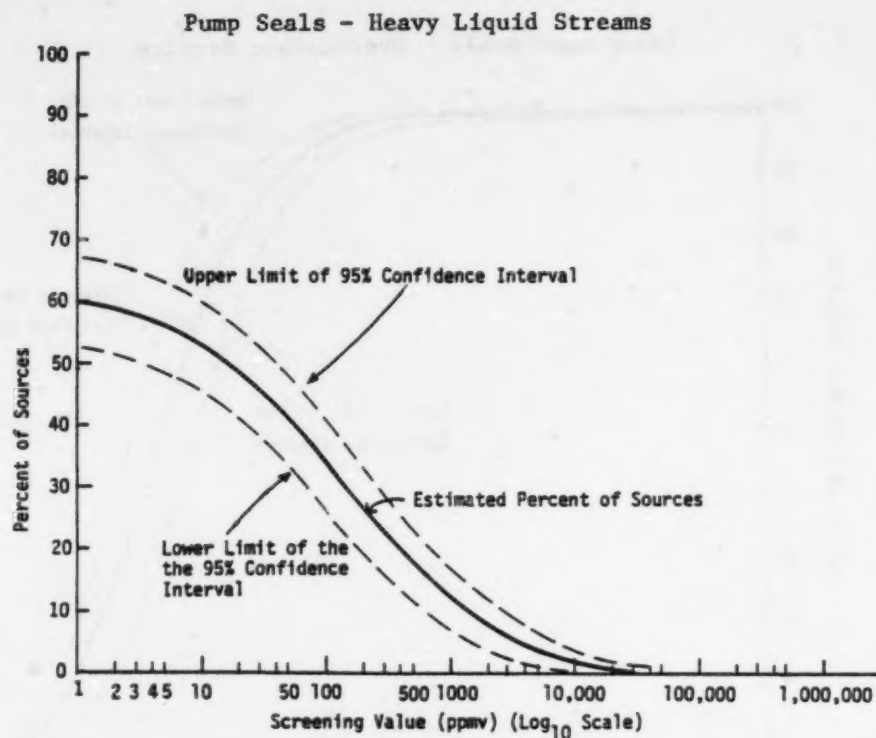


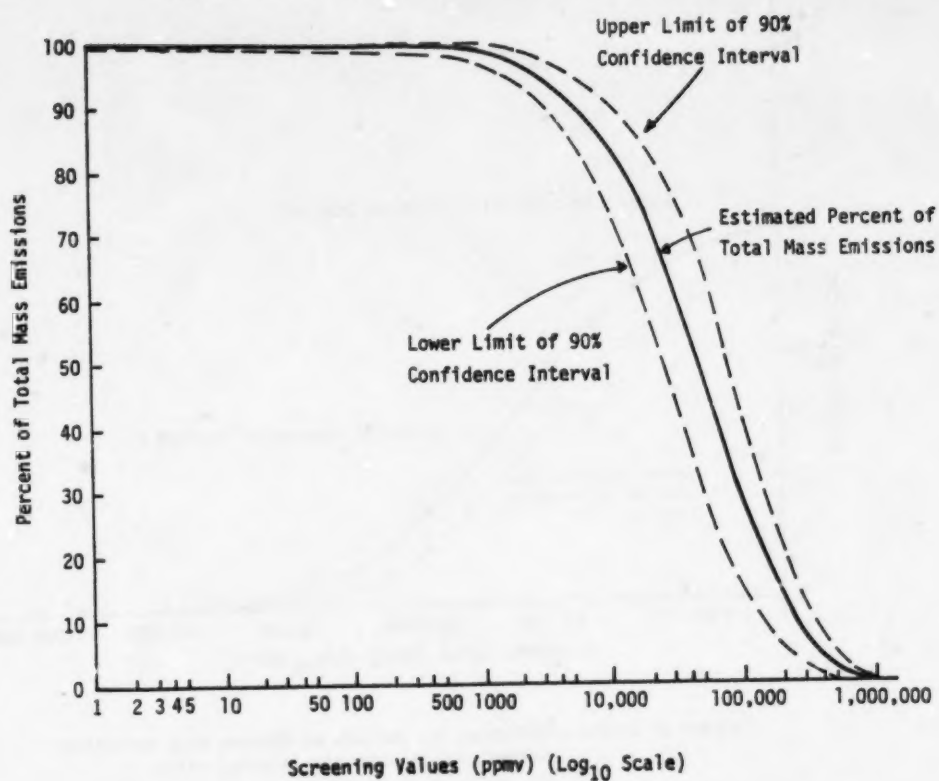
Figure 4-10A. Cumulative Distribution of Total Emissions by Screening Values - Pump Seals - Light Liquid Streams



Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

Figure 4-11B. Cumulative Distribution of Sources by Screening Values - Pump Seals - Heavy Liquid Streams

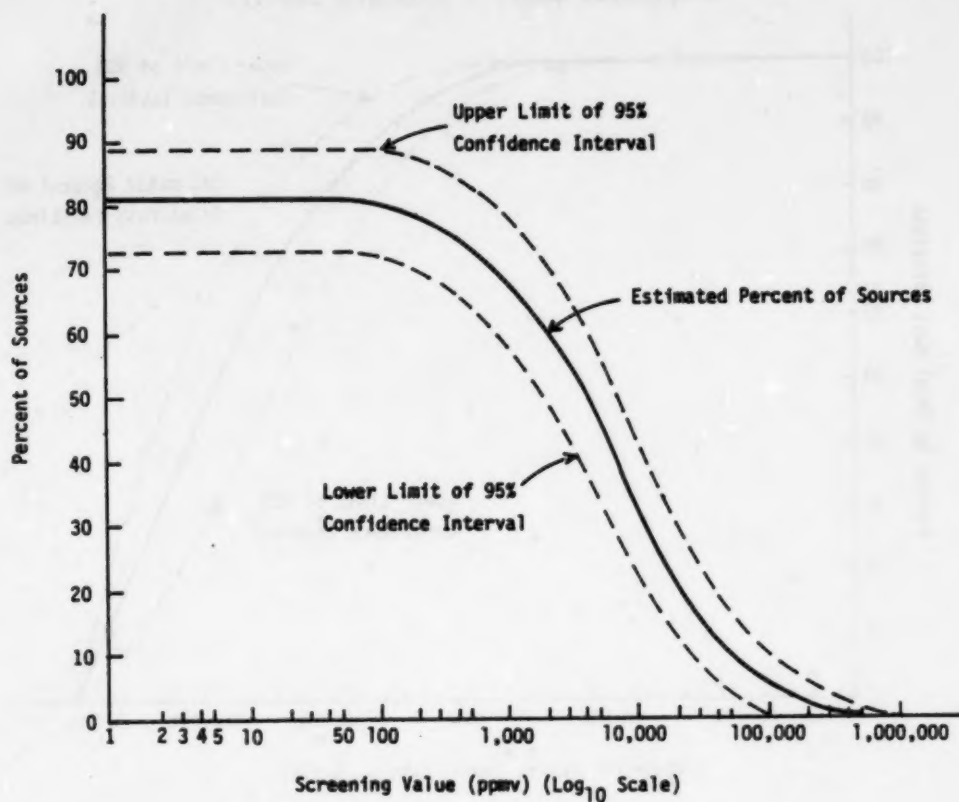
Compressor Seals - Hydrocarbon Service



Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.

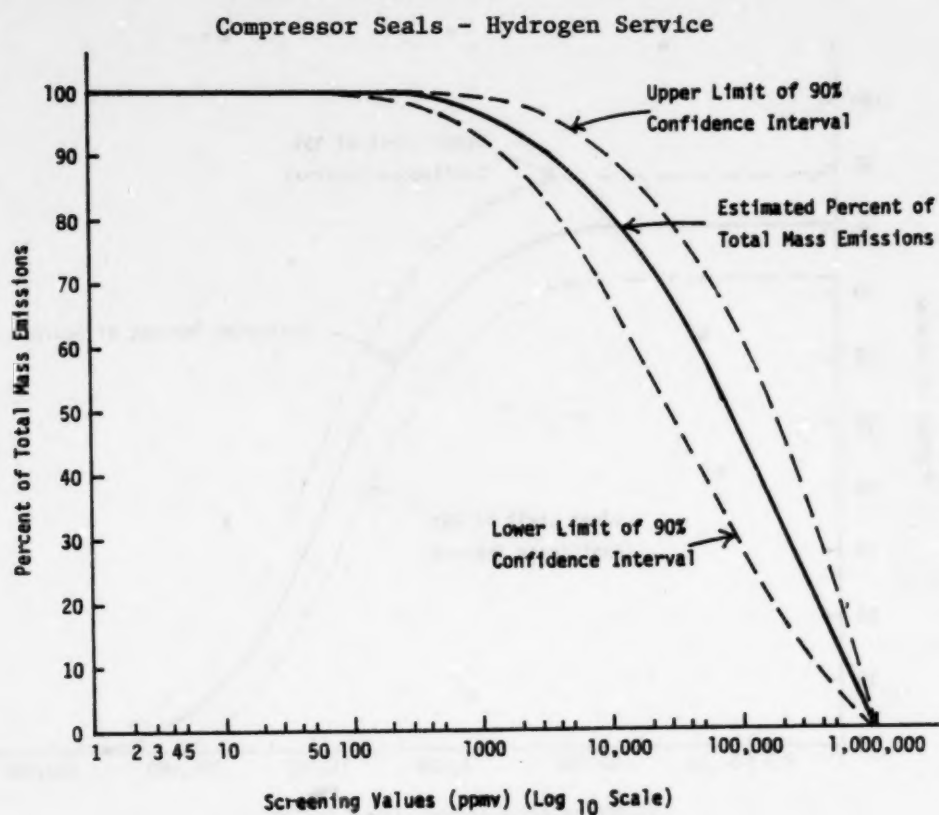
Figure 4-12A. Cumulative Distribution of Total Emissions by Screening Values - Compressor Seals - Hydrocarbon Service

Compressor Seals - Hydrocarbon Service



Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

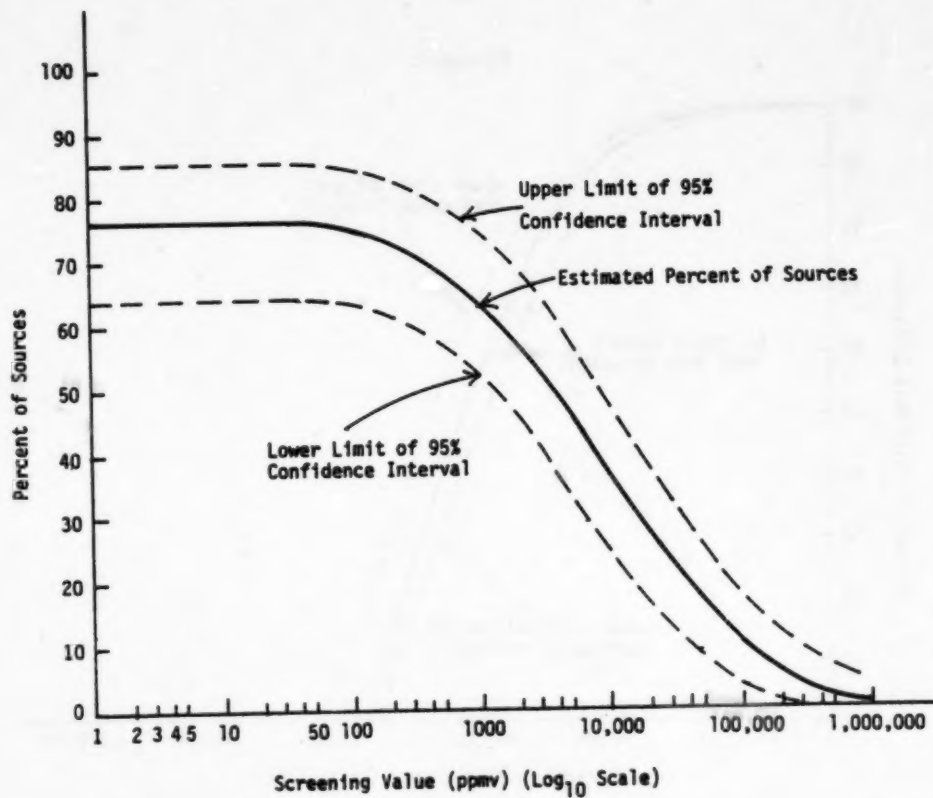
Figure 4-12B. Cumulative Distribution of Source by Screening Values - Compressor Seals - Hydrocarbon Service



Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.

Figure 4-13A. Cumulative Distribution of Total Emissions by Screening Values - Compressor Seals - Hydrogen Service

Compressor Seals - Hydrogen Service



Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

Figure 4-13B. Cumulative Distribution of Sources by Screening Values - Compressor Seals - Hydrogen Service

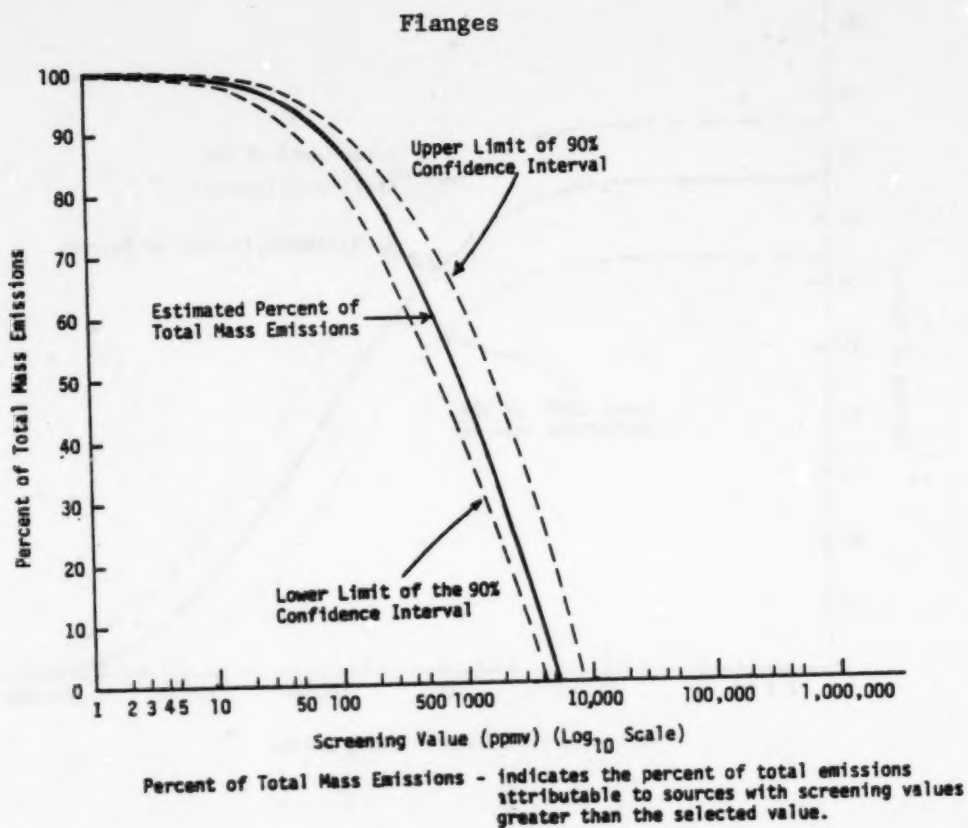
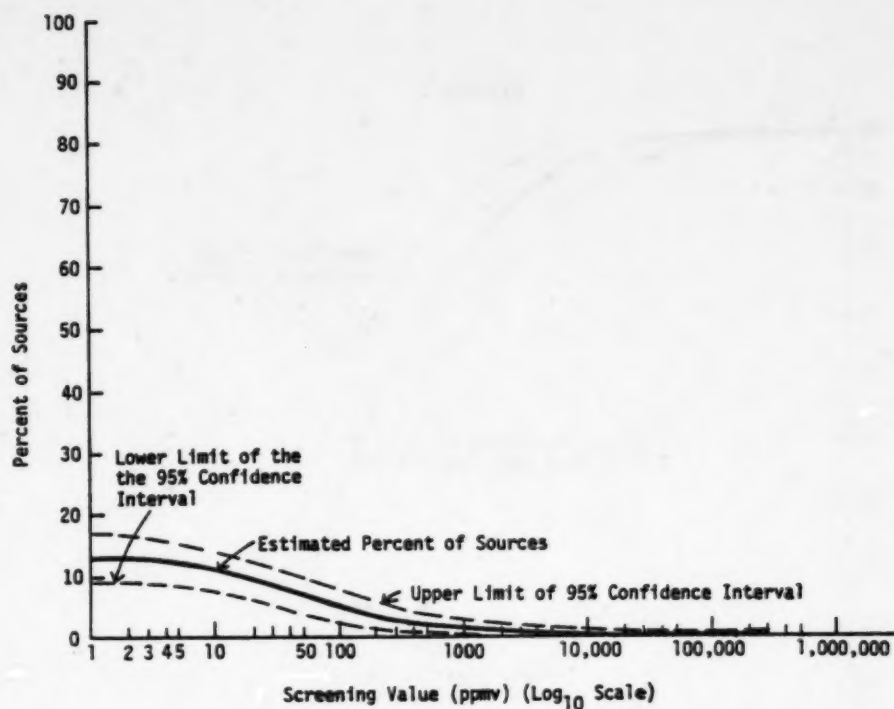


Figure 4-14A. Cumulative Distribution of Total Emissions by Screening Values - Flanges

Flanges



Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

Figure 4-14B. Cumulative Distribution of Sources by Screening Values - Flanges

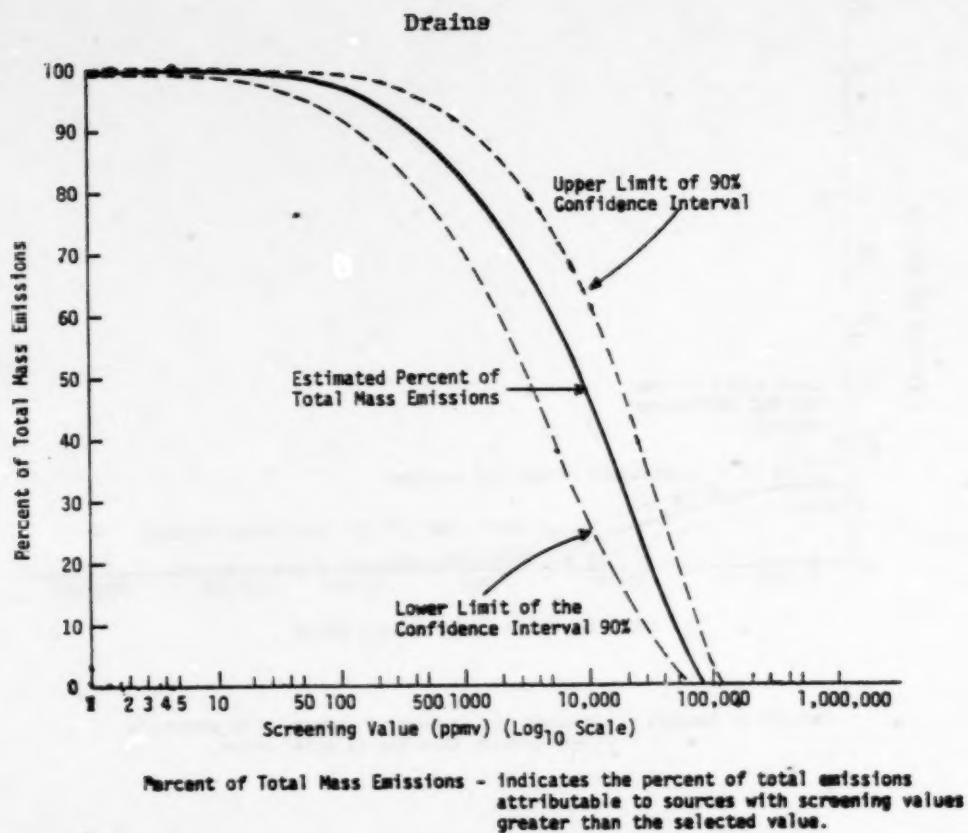
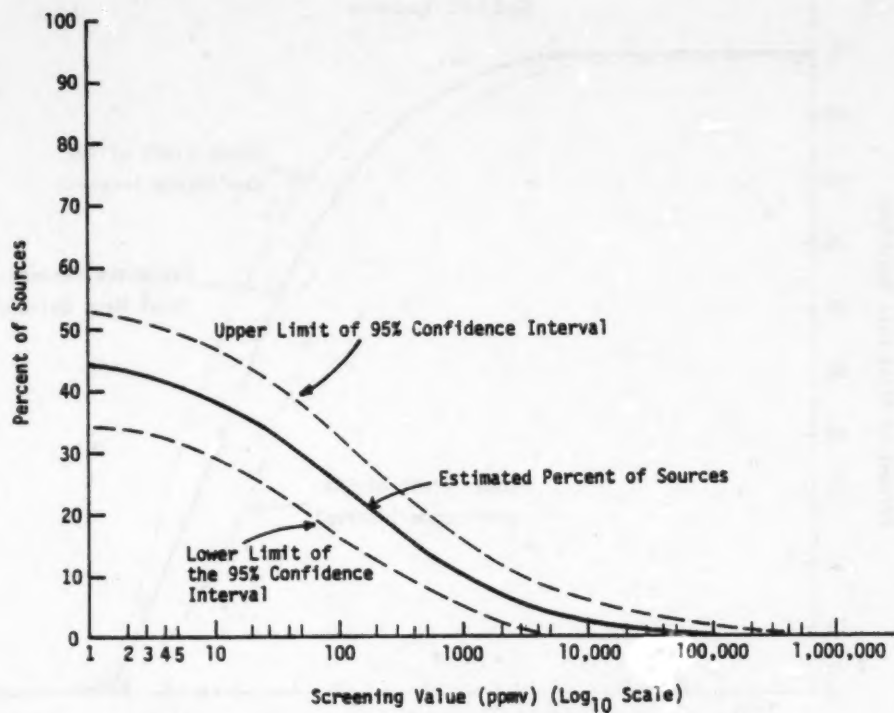


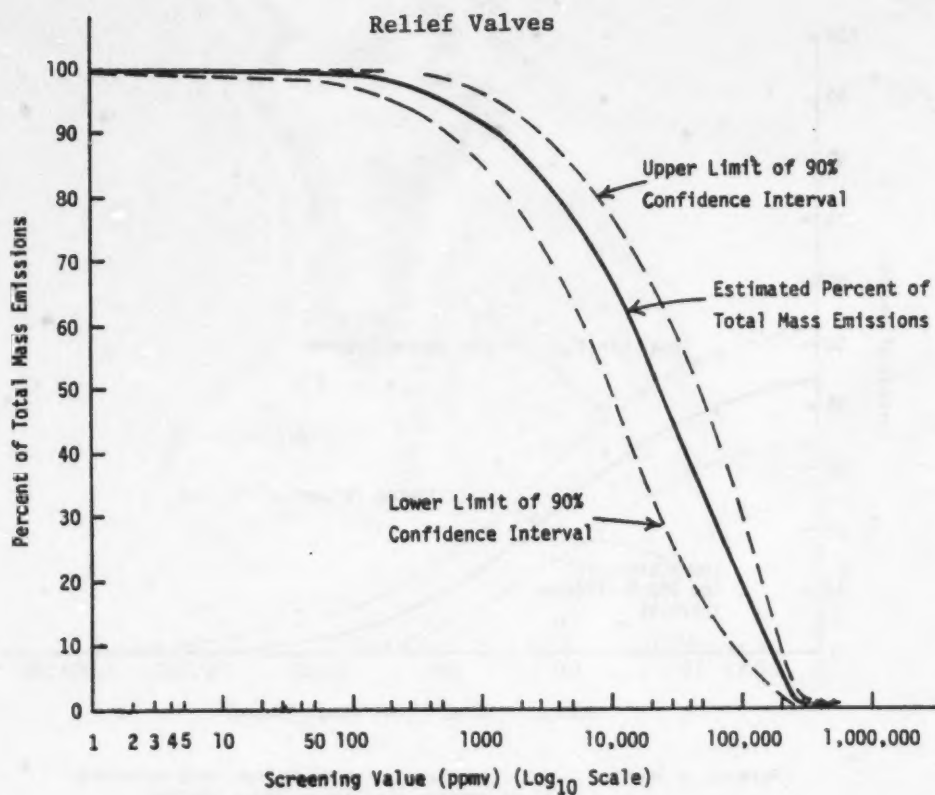
Figure 4-15A. Cumulative Distribution of Total Emissions by Screening Values - Drains

Drains



Percent of Sources - indicates the percent of sources with screening values greater than the selected source.

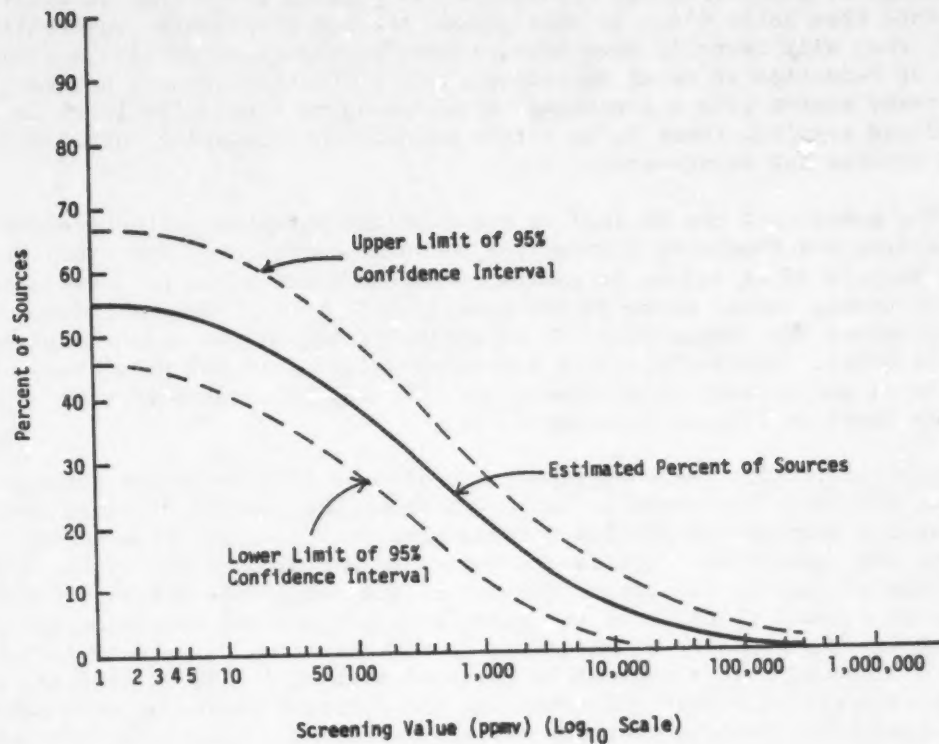
Figure 4-15B. Cumulative Distribution of Sources by Screening Values - Drains



Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.

Figure 4-16A. Cumulative Distribution of Total Emissions of Screening Values - Relief Valves

Relief Valves



Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

Figure 4-16B. Cumulative Distribution of Sources by Screening Values - Relief Valves

The nomographs must be used with caution. As discussed earlier, the correlation between screening values and actual leak rates is imperfect. Because of this, values obtained from the nomographs for percent of total sources and percent of total emissions at a specific screening value will not exactly match similar values in Table 4-4, if one converts screening values to leak rates. In most cases, the nomographs will indicate a higher percentage of sources being responsible for a given percentage of total emissions than Table 4-4. In this sense, the nomographs are conservative (i.e., they will identify more sources than necessary to achieve a given level of reduction on total emissions). In a practical sense, however, unless every source with a screening value exceeding a specific level is bagged and sampled, there is no better method than screening for identifying sources for maintenance.

The nomographs can be used to evaluate the potential effectiveness of maintaining and repairing sources for reducing emissions. For example, approximately 5% of valves in gas/vapor stream service can be expected to have screening values above 50,000 ppmv (Figure 4-7B). However, these 5% of the valves are responsible for an estimated 92% of the mass emissions (Figure 4-7A). Similarly, for a screening value of 10,000 ppmv, the percent of sources and percent of emissions are 10%, and 98%, respectively. (See example lines on Figures 4-7A and 4-7B).

Analyses, using the nomographs, can also be done for other sources and process streams. For example, Table 4-5 shows the percent of emissions for various sources and process streams when the upper 10% of screened sources are considered. Confidence intervals are also shown. Table 4-5 is presented only to illustrate the use of the nomographs and to emphasize the fact that a small fraction of the sources within any one source category account for the majority of emissions in that category. There is no intent here to prejudge that a reasonable level of control is 10% of sources, or any other specific number. Ultimately, the decision regarding reasonable control will be based on reducing overall emissions. Therefore, percentage reduction goals for each source category may be different. The variations in source emissions from a hypothetical refinery (Table 4-3) further illustrates the need to develop different emission reduction goals for various source categories.

In summary, Figures 4-7 through 4-16 present continuous distributions of the percent of emissions and sources versus specific screening values. These figures can be used to estimate the reduction in emissions which could ideally occur if a given percentage of leaking sources were repaired. It is emphasized that these figures represent an amalgamation of data from nine refineries (thirteen for compressor seals and relief valves) and do not represent any single refinery. Therefore, these results must be used with caution when analyzing a specific refinery or process unit.

TABLE 4-5. PERCENT OF TOTAL MASS EMISSIONS RELEASED BY THE
UPPER¹ TEN PERCENT OF SCREENED SOURCES

SOURCE	MINIMUM SCREENING VALUE (ppmv)	95% CONFIDENCE INTERVAL FOR PERCENT OF SOURCES	PERCENT OF TOTAL EMISSIONS 90% CONFIDENCE INTERVAL	
			MEAN	
VALVES				
Gas/Vapor	11,000	(7 , 13)	98	(97 , 99)
Light Liquid/Two-Phase	12,000	(7 , 12)	82	(78 , 86)
Heavy Liquid	120	(5 , 15)	77	(69 , 85)
PUMP SEALS				
Light Liquid	44,000	(7 , 13)	68	(63 , 75)
Heavy Liquid	1,500	(5 , 15)	60	(47 , 78)
COMPRESSOR SEALS				
Hydrocarbon Service	50,000	(4 , 18)	47	(31 , 64)
Hydrogen Service	120,000	(3 , 15)	41	(23 , 57)
FLANGES	17	(7 , 13)	98	(97 , 99)
DRAINS	1,200	(4 , 15)	78	(68 , 90)
RELIEF VALVES	4,500	(4 , 18)	80	(65 , 87)

¹ The upper ten percent of screened sources is defined as the ten percent of sources having the highest screening values.

Appendix A. Emission Factor Development - Statistical Considerations

Because of the high degree of skewness in the distribution of nonmethane leak rates from baggable sources, conventional statistics are inadequate for efficient estimation of emission factors and their variances. In addition to the skewness, a large percentage of the sources studied were considered "non-leaking." These sources affect the emission factor and therefore must be considered in developing estimates for these factors. Another statistical problem which had to be addressed in developing the emission factors was the estimation of leak rates for sources which screened greater than or equal to 200 ppmv but were not sampled.

A.1 Estimating Emissions for Nonsampled Sources

Due to time and equipment constraints, it was not always possible to sample all sources that screened greater than 200 ppmv. At the fifth refinery, a sampling strategy was developed to reduce the sampling workload. All sources screening greater than 10,000 ppmv were sampled, but only one-fourth of the valves and pumps with screening values between 200 and 10,000 ppmv were sampled. In order not to bias the distribution of leaking sources, it was necessary to develop estimated values for all sources screening greater than 200 ppmv and not sampled. The number of sources sampled and estimated for each source type is shown in the following table:

Baggable Source Type	Total Sources Sampled or Screened >200 ppmv	Sources Sampled	Sources to be Estimated
Valves	627	474	153
Pump Seals	382	281	101
Compressor Seals			
Hydrocarbon Service	102	83	19
Hydrogen Service	69	60	9
Flanges	62	43	19
Drains	49	28	21
Relief Valves	58	31	27

Least-squares regression analyses were done for each device type, regressing the logarithm of the nonmethane leak rate on the logarithm of the maximum screening reading. Both the original screening value and rescreening values (taken closer to the time of sampling for leak rate) were evaluated and a "best" equation was selected for each device as summarized in Table A-1.

Using the equations in Table A-1, predicted log-nonmethane leak rates were computed for each source not sampled with a screening value greater than or equal to 200 ppmv. Leak rates (lb/hr) were then computed using

$$\text{leak rate} = \exp 10 [\text{Log leak} + z (\text{standard error of estimate})],$$

TABLE A-1. PREDICTION EQUATIONS FOR NONMETHANE LEAK RATES
BASED ON MAXIMUM TLV SCREENING OR RESCREENING VALUES

SOURCE TYPE	LEAST - SQUARES EQUATION	NUMBER OF DATA PAIRS	CORRELATION COEFFICIENT (r)	STANDARD ERROR OF ESTIMATE
Valves	$\text{LOG(NMLK)} = -5.41 + 0.88 \text{ LOG(MXTLV-RS)}$	177	0.78	0.736
Pump Seals	$\text{LOG(NMLK)} = -4.64 + 0.89 \text{ LOG(MXTLV-RS)}$	171	0.68	0.820
Compressor Seals:				
Hydrocarbon Service	$\text{LOG(NMLK)} = -4.77 + 0.92 \text{ LOG(MXTLV-RS)}$	48	0.58	0.791
Hydrogen Service	$\text{LOG(NMLK)} = -3.66 + 0.44 \text{ LOG(MXTLV-S)}$	44	0.36	0.884
Flanges	$\text{LOG(NMLK)} = -5.11 + 0.84 \text{ LOG(MXTLV-S)}$	47	0.74	0.535
Drains	$\text{LOG(NMLK)} = -5.02 + 1.16 \text{ LOG(MXTLV-S)}$	60	0.72	0.807
Relief Valves	$\text{LOG(NMLK)} = -4.47 + 0.87 \text{ LOG(MXTLV-RS)}$	53	0.78	0.637

NMLK - Nonmethane leak rate (lb/hr)
MXTLV-S - Maximum value - original screening (ppmv)
MXTLV-RS - Maximum value - rescreening (ppmv)
LOG - Logarithm, base 10

where z is a random number from a standard-normal distribution. The use of the random number is an attempt to yield a predicted distribution of leak rates which would approximate the distribution if all sources were sampled. No bias correction factor is needed in going from the Log to arithmetic scale since the mean leak rate is not being predicted. These predicted leak rates were used in further analyses and development of emission factors.

Because the true leak rate/screening relationship is unknown, there is a potential bias introduced when these predicted leak rates are used in developing emission factors. The potential bias is proportioned to the standard error of the estimates divided by the number of data pairs used to develop the equation. The impact of the bias on emission factors depends on the percent of sources leaking. The potential bias was found to be less than one percent for all source types except compressor seals and relief valves. The potential biases were estimated to be $\pm 9.6\%$ of the emission factor for relief valves, $\pm 17.5\%$ for compressor seals in hydrocarbon service, and $\pm 7.1\%$ for compressor seals in hydrogen service. These potential biases were taken into consideration in developing confidence intervals as discussed in Section A.3.

A.2 Statistical Distribution Models for Leak Rates

A lognormal distribution was used to model the distribution of leaking sources. This distribution has the property that when the original data are transformed by taking natural logarithms, the transformed data will follow a normal distribution. The lognormal distribution is often appropriate when the standard error of an individual value is proportional to the magnitude of the value. The form of the lognormal distribution is as follows:

$$f(x) = \frac{\exp\left[-\frac{(\ln x - \mu)^2}{2\sigma^2}\right]}{x\sigma\sqrt{2\pi}} \quad \text{for } 0 < x < \infty$$

$$= 0 \quad \text{for } x \leq 0$$

$$\text{Mean} = \exp\left[\mu + \frac{\sigma^2}{2}\right]$$

$$\text{Variance} = \exp[2\mu + 2\sigma^2] - \exp[2\mu + \sigma^2]$$

In order to develop estimates for emission factors, the non-leaking sources (leak rate assumed equal to zero) also had to be modeled. A mixed distribution, specifically a lognormal distribution with a discrete probability mass at zero, was used for this purpose. Letting ρ equal the fraction of nonleaking sources in the population, this distribution has the following form:

$$f(x) = \frac{(1-\rho) \exp\left[-\frac{(\ln x - \mu)^2}{2\sigma^2}\right]}{x\sigma\sqrt{2\pi}} \quad \text{for } 0 < x < \infty$$

$$= \rho \quad \text{for } x = 0$$

$$= 0 \quad \text{for } x < 0$$

$$\text{Mean} = (1-\rho) \exp\left[\mu + \frac{\sigma^2}{2}\right]$$

$$\text{Variance} = (1-\rho) [\exp(2\mu + \sigma^2)] [\exp(\sigma^2) - (1-\rho)]$$

Efficient estimates of the mean and variance of the population modeled by this mixed distribution have been developed [Finney (1941), Aitchison (1955)]. These estimates are as follows:

The best, unbiased estimator of the population mean emission rate is

$$m = \left[\left(1 - \frac{r}{n}\right) \exp\left[\left(\bar{x}\right)\right] g\left(\frac{s^2}{2}\right) \right]$$

and the best, unbiased estimator of the population variance of the emission rates is

$$v = \left[\left(1 - \frac{r}{n}\right) \exp(2\bar{x}) [g(2s^2) - \left(1 - \frac{r}{n-1}\right) g\left(\frac{n-r-2}{n-r-1} s^2\right)] \right]$$

where n = number of sources screened,

r = number of sources screened <200 ppm or with measured leak <10⁻⁵ lbs/hr

$m = n-r$ = number of "leaking" sources,

$g(t)$ = infinite series

$$= 1 + \frac{(m-1)t}{m} + \frac{(m-1)^3 t^2}{m^2 2! (m+1)} + \frac{(m-1)^5 t^3}{m^3 3! (m+1)(m+3)} + \dots$$

$\bar{x}$ = average of the logarithm of leaking sources

$$= \sum_{i=1}^{n-r} \ln(\text{nonmethane leaks}) / (n-r)$$

s^2 = variance of the logarithm of leaking sources

$$= \sum_{i=1}^{n-r} [\ln(\text{nonmethane leaks}) - \bar{x}]^2 / (n-r-1)$$

The mean and variance formulas hold whenever there is more than one leaking source ($n-r > 1$). When only one leaking source is identified, the following estimates are appropriate:

$$\text{mean} = \frac{x_1}{n} \quad \text{and} \quad \text{variance} = \frac{x_1^2}{n},$$

where x_1 is the single measured leak. If no leaks are found ($r=n$), then the best estimate for both the mean and variance is zero.

Computer programs were developed for these estimators and the estimator for the mean was used for all emission factors presented in this publication. Finney (1941) showed that this estimator is more than twice as efficient as the arithmetic mean for data distributed similarly to the leak rates from baggable sources.

Since data distributed lognormally can be transformed to a normal distribution by taking natural logarithms of the data, the distribution assumptions can be tested by examining distributions of the Log leak rates. Histograms displaying these distributions were constructed for all important source type and process stream classifications. The data for most sources appeared to adequately approximate a normal distribution. The compressor seals data from hydrocarbon service and the heavy stream data for pump seals both appeared skewed to the left. Compressor seals with sampled leak rates less than 10^{-3} were considered as negligible (zero) to minimize this skewness.

To statistically test the assumption of a normal distribution for the log-leak rates, skewness and kurtosis statistics were computed for each data group and tested for departures from their expected values of zero in a normal distribution. The following table summarizes these statistics.

<u>Source Type/ Stream Group</u>	<u>Number of Leaking Sources</u>	<u>Skewness</u>	<u>Kurtosis</u>
Valves (all)	627	0.02	-0.03
Gas/Vapor Streams	200	0.17	-0.36
Light Liquids/Two-Phase	372	-0.15	-0.25
Heavy Liquids	35	0.37	-0.73
Pump Seals (All)	382	-0.07	-0.30
Light Liquids	300	0.01	-0.38
Heavy Liquids	66	-0.77*	0.06
Compressor Seals			
Hydrocarbon Service	99	-0.65*	0.37
Hydrocarbon Service	69	-0.29	0.69
Flanges	62	0.39	0.20
Drains	49	-0.04	-0.47
Relief Valves	42	-0.22	-0.26

* probability <.10 given a normal distribution.

Only two of the twelve cases indicated significant lack of normality, confirming the conclusions from the histograms. It was decided that these two cases did not merit fitting of an alternative distribution at this time. These distributions will be addressed in the final report when other potential correlating variables are studied.

A.3 Confidence Intervals for Percent Sources Leaking and for Emission Factors

Confidence intervals for the percent of leaking sources were computed using the Binomial Distribution. The Binomial is used to model data when a random sample is selected and each item is classified into one of two categories (leaking or non-leaking here). Exact confidence limits (level $1-\alpha$) for the estimate of percent leaking can be obtained by iteration solving for P_L in

$$\sum_{i=k}^n \binom{n}{i} P_L^i (1 - P_L)^{n-i} = \frac{\alpha}{2} \text{ for the lower limit and for } P_U \text{ in}$$

$$\sum_{i=0}^k \binom{n}{i} P_U^i (1 - P_U)^{n-i} = \frac{\alpha}{2} \text{ for the upper limit}$$

where n = number of sources screened and k = number of leaking sources. Tables of these solutions, available for most cases, were used to develop 95% confidence intervals reported in this publication and for computing 97.5% confidence intervals which were used in developing confidence intervals for emission factors. 97.5% was selected so that 95% confidence intervals for emission factors would result when the estimated percent leaking was combined with the estimated mean leak rate ($0.975 \times 0.975 \approx 0.95$)

Patterson (1966) described how confidence intervals for the mean from a lognormal distribution can be computed using estimators developed by Finney (1941). 97.5% confidence intervals were computed for the average, $\bar{y}$, of the transformed data, $y = \ln(\text{leak})$, using

$$C_L = \text{lower limit} = \bar{y} - 2.24 [s^2/(n-r)]^{1/2} \text{ and}$$

$$C_U = \text{upper limit} = \bar{y} + 2.24 [s^2/(n-r)]^{1/2}$$

where s^2 is the variance of the transformed data and $n-r$ is the number of leaking sources. Then, following Patterson's arguments, confidence intervals for the mean leak rate can be computed using:

$$\text{lower limit} = \exp [C_L] g(s^2/2) \quad \text{and}$$

$$\text{upper limit} = \exp [C_U] g(s^2/2)$$

where $g(t)$ is the series given in Section A.2.

To obtain 95% confidence limits for the emission factors, the confidence limits for the percent leaking and for the mean leak rate were combined as follows:

lower 95% limit for emission factor = $P_L (C_L)$

upper 95% limit for emission factor = $P_u (C_u)$

These confidence intervals are conservative in the sense that 95% is a lower bound for the confidence coefficient for the intervals. The confidence intervals should be interpreted as follows:

When we state that the true emission factor falls within the limits computed as described above, we expect to be correct at least 95% of the time.

The confidence intervals consider random sampling variation and random test error, with no adjustments for potential bias in the sampling and analytical methods. Standards sampled and analyzed at most refineries have not indicated any significant bias at this time, but some results have shown low recoveries (<100%). A bias factor, if significant, will be computed when all standards data becomes available. To account for potential low bias at this time, the upper confidence limits were increased 5% as follows:

adjusted upper 95% confidence limit = $P_u (C_u) + .05 (P_u (C_u))$

In addition to the above adjustment for all source types, the upper and lower confidence intervals for compressor seals and relief valves were adjusted to compensate for the potential bias due to estimating leak rates as discussed in Section A.1. The limits were expanded an additional 9.6% for relief valves, 17.5% for compressor seals in hydrocarbon service and 7.1% for compressor seals in hydrogen service.

A.4 Development of Nomographs

Three types of nomographs were developed as part of this report:

- (1) Predicting mean leak rate from screening values
- (2) cumulative percent of sources for increasing screening values
- (3) cumulative percent of total emissions for increasing screening values.

This section describes how these nomographs were constructed.

A.4.1 Predicting Mean Leak Rate from Screening Values

Section A.1 describes least-square linear regression equations developed for predicting leaks from non-sampled sources in the data base with screening values greater than 200 ppmv. For prediction purposes outside the data base, a statistical analysis of covariance was done to determine if different

equations were required for the various source types and stream groupings. The results of this analysis showed that one equation using the maximum rescreening value was adequate for all stream types for pumps, compressors, drains, and relief valves. This does not imply that the leak rate versus screening relationship is identical for these devices, but that the differences are small relative to the random scatter of the data. For valves and flanges, separate equations were required for the gas/vapor streams and the light liquid/tw-phase and heavy liquid streams.

The resulting equations are as follows:

I. Valves and Flanges - Gas/Vapor Streams

$\text{LOG}_{10} (\text{NMLEAK}) = -7.0 + 1.16 \text{ LOG}_{10} (\text{Max-rescreening})$
 correlation = 0.71 number of data pairs = 106
 standard error of estimate = 0.91 $\text{LOG}_{10} (\text{NMLEAK})$
 95% confidence interval for intercept (-7.9, -5.9)
 95% confidence interval for slope (0.94, 1.4)
 scale bias correction factor = 8.59

II. Valves and Flanges - Light Liquid/Two-Phase and Heavy Liquid Streams

$\text{LOG}_{10} (\text{NMLEAK}) = -4.8 + 0.76 \text{ LOG}_{10} (\text{Max-rescreening})$
 correlation = 0.76 number of data pairs = 147
 standard error of estimate = 0.65 $\text{LOG}_{10} (\text{NMLEAK})$
 95% confidence interval for intercept (-5.2, -4.3)
 95% confidence interval for slope (0.66, 0.87)
 scale bias correction factor = 3.00

III. Pump Seals, Compressor Seals, Drains, Relief Valves

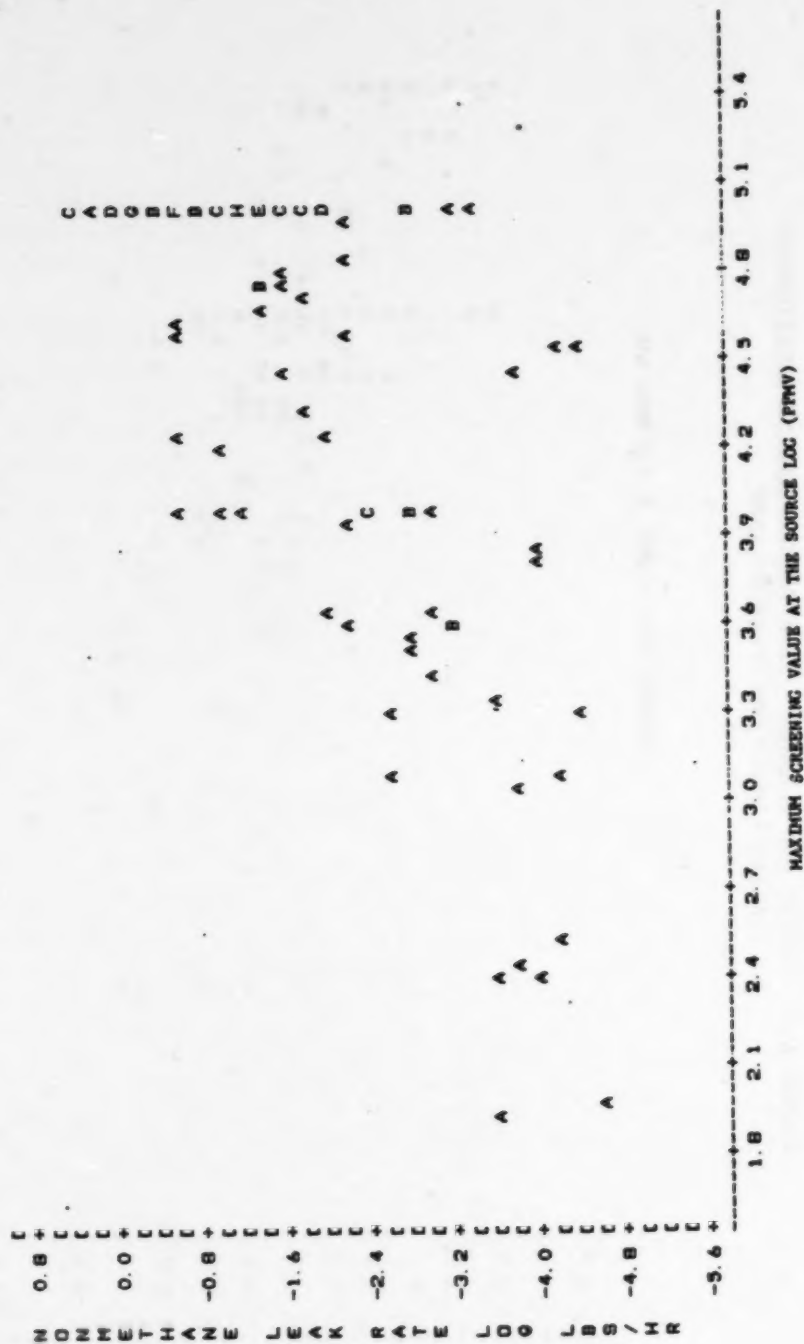
$\text{LOG}_{10} (\text{NMLEAK}) = -4.0 + 0.73 \text{ LOG}_{10} (\text{Max-Rescreening})$
 correlation = 0.62 number of data pairs = 168
 standard error of estimate = 0.82 $\text{LOG}_{10} (\text{NMLEAK})$
 95% confidence interval for intercept (-4.5, -3.4)
 95% confidence interval for slope (0.59, 0.87)
 scale bias correction factor = 4.90

The data used to develop these equations are shown in Figures A-1 through A-3. These equations were used to develop the three sets of nomographs shown in Figures 4-1 to 4-6 of this report. Although the equations were developed on a logarithmic scale, the nomographs are shown on an arithmetic scale for ease in reading and interpolation. Predicting the arithmetic mean leak rate for a given screening value is similar to predicting the mean from a lognormal distribution as discussed in Section A.2. The mean value for a given screening value on the nomograph was computed as follows:

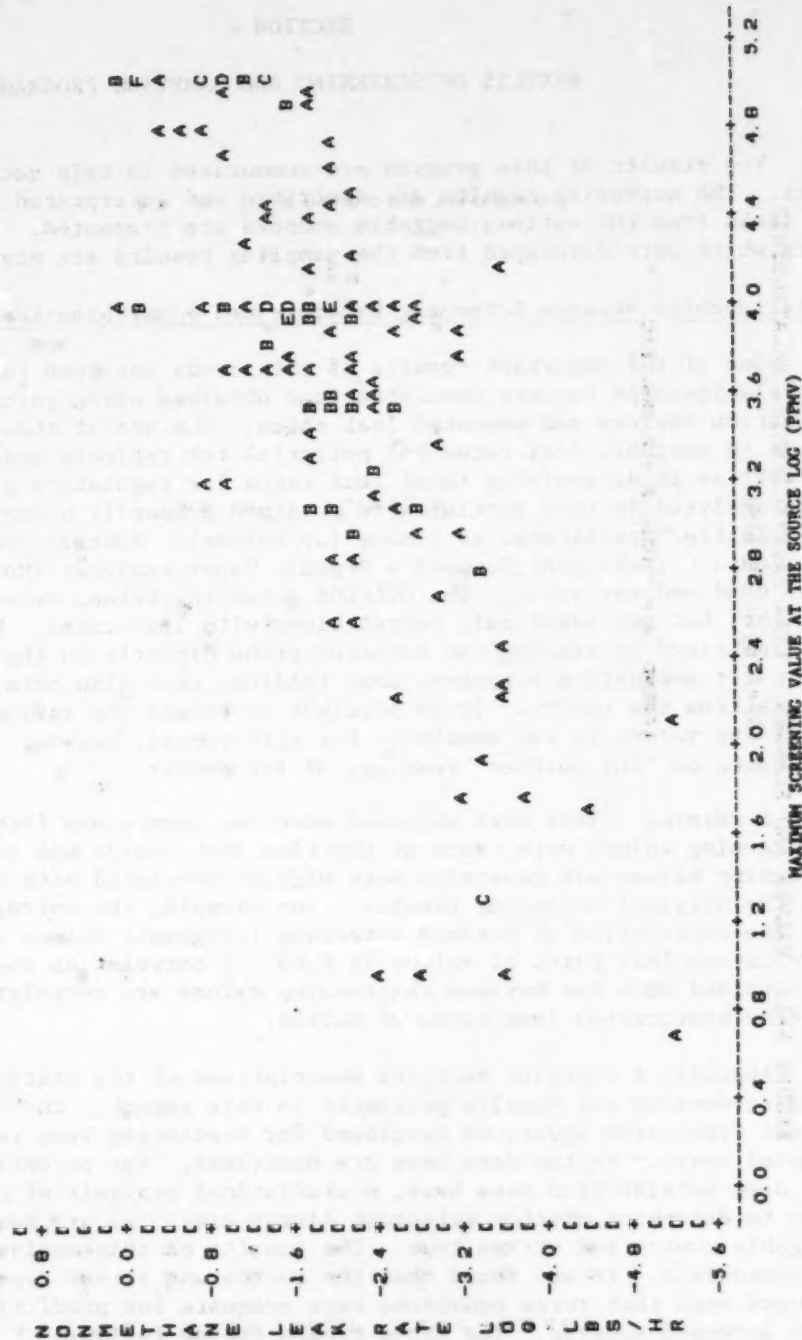
$$\begin{aligned} \text{mean} &= \exp_{10} [B_0 + B_1 \text{ LOG}_{10}(\text{screening})] \quad g\left(\frac{\text{SE}^2}{\text{Ln}2}\right) \\ &= (10)^{B_0} (\text{screening value})^{B_1} (\text{scale bias correction factor}) \end{aligned}$$

FIGURE A-1. VALVES AND FLANGES - LEAK RATE/SCREENING RELATIONSHIP
Gas/Vapor Streams

LEGEND: A = 1 OBS, B = 2 OBS, ETC.



LEGEND: A = 1 OBS, B = 2 OBS, ETC.



where B_0 - Log regression intercept
 B_1 - Log regression slope
 $SE_{\ln}$ - standard error of estimate in natural Log scale
 $g(t)$ - series described in Section A.2.

90% confidence intervals for the predicted mean leak for a given screening value were computed in a similar manner to the confidence intervals for the mean leak rate as described in Section A.2.

A.4.2 Cumulative Percent of Sources for Increasing Screening Values

The nomographs in Figures 4-7B to 4-16B of the report contain the estimated cumulative distribution of Log screening values. The nomographs show 100% minus the cumulative percent, or the estimated percent of sources which would have screening values greater than any particular screening value. These cumulative distribution functions were estimated by fitting a lognormal distribution, as described in Section A.2, to the screening data and then generating the cumulative distribution.

There was some difficulty in fitting the lognormal distribution to the screening values. Figure A.4 shows a typical histogram of Log screening values for valves from gas streams. The histogram appears to approximate a normal distribution adequately up to 10,000 ppm (4.0 on LOG_{10} scale). The spike at 10,000 ppm was due to the inability of the screening device to measure beyond 10,000 without a dilution probe. The dilution probe was used in only a few cases in the screening process during this program.

To overcome the bias caused by this spike, only Log screening values less than 4.0 were used to estimate the parameters of this distribution. Formulas from "censored" normal distribution theory (Cohen, 1959) were then used to arrive at unbiased estimates of the entire distribution. These estimates were used to generate the cumulative distribution function for each source type/process stream grouping.

Confidence intervals for these cumulative functions were obtained using the Binomial Distribution as in Section A.3. The 95% confidence interval for individual probabilities were approximated using

$$\hat{p} \pm 1.96 [\hat{p} (1-\hat{p}) / n]^{1/2}$$

where $\hat{p}$ is the estimated cumulative percent and n is the number of screening values for each particular source type and stream group.

Assuming that the sources screened approximate a random sample from the population of a particular source type, these confidence intervals can be interpreted as follows:

When we state that the true percent of sources in the population which have screening values greater than any selected screening value lies within the confidence bounds, we expect to be correct about 95% of the time.

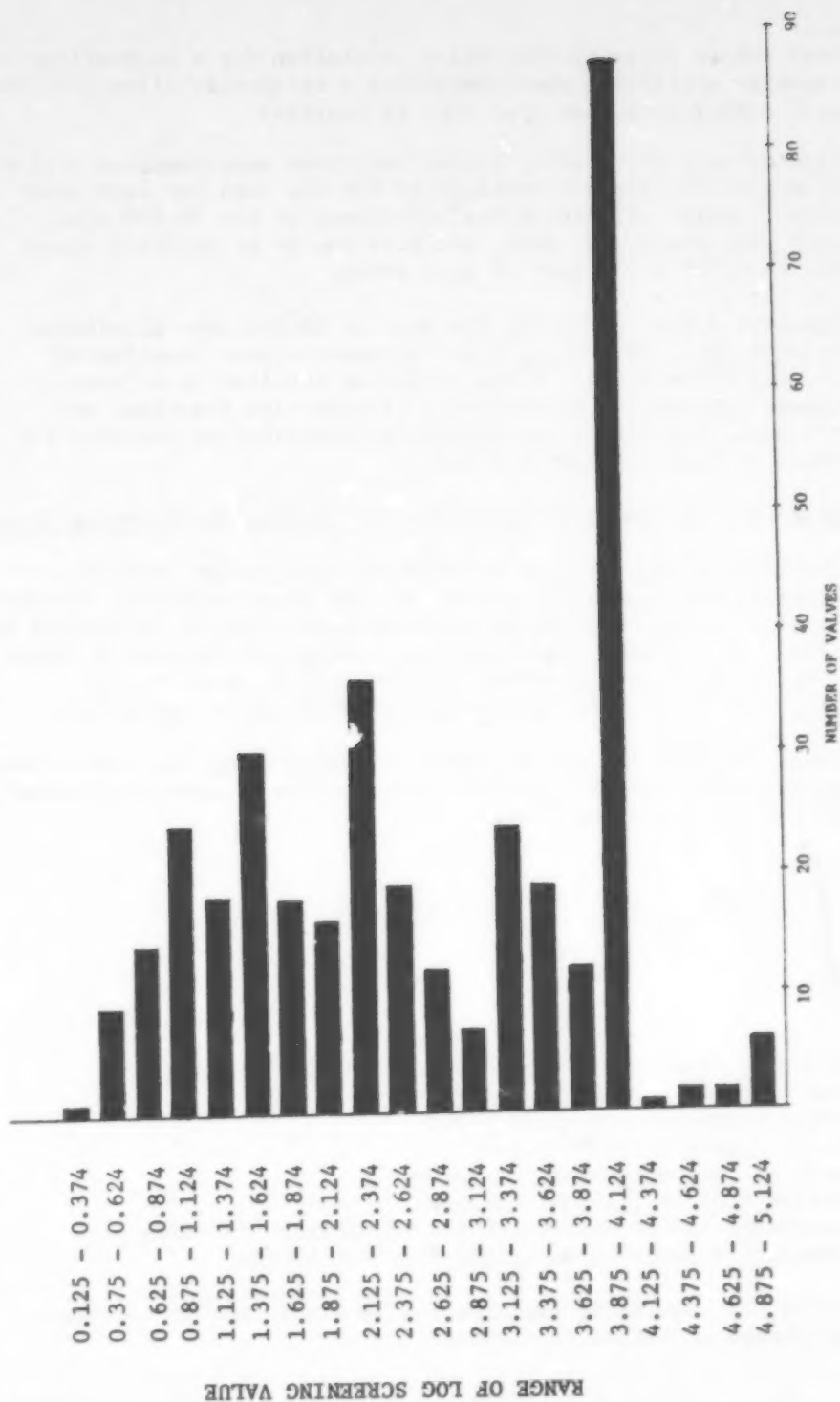


Figure A-4.
DISTRIBUTION OF LOG ₁₀ (MAX SCREENING VALUE)
Valves - Gas/Vapor Streams

Note that these limits apply to the entire population for a source type and are not necessarily applicable when addressing a particular situation concerning a small number (say less than 100) of sources.

The estimated cumulative distribution functions were compared with the sample distribution function and appeared to fit the data for each case except compressor seals. Discrepancies were found at the 10,000 ppmv screening value, in almost all cases, but this was to be expected since the sample function had a big jump at this point.

For compressor seals, censoring the data at 10,000 ppmv eliminated 64% of the observations, so the lognormal parameters were reestimated using all the data as recorded. These estimates resulted in a "better" agreement between the sample and estimates distribution function, and were therefore used to generate the cumulative distribution function for compressor seals in both types of service.

A.4.3 Cumulative Percent of Total Emissions for Increasing Screening Values

The nomographs in Figures 4-7A to 4-16A of this report contain a function estimating the cumulative percent of the total emissions attributable to each particular source type/stream group as a function of increasing Log screening values. As before, 100% minus the cumulative function is shown so that the percent of total emissions attributable to sources with screening values above any selected screening value can be determined.

This cumulative function was estimated by integrating the leak/screening regression relationship over a lognormal distribution of screening values. This function has the following form:

$$CF = \int_0^{S_0} \frac{C(10)^{B_0} (x)^{B_1}}{x\sigma \sqrt{2\pi}} \exp \left[-\frac{(\ln x - u)^2}{2\sigma^2} \right] dx$$

where S_0 - selected upper screening value for integration
 C - Log/arithmetic scale bias correction factor
 B_0 - Log_{10} regression intercept term
 B_1 - Log_{10} regression slope term
 u - mean of the Log_e (screening values)
 σ^2 - variance of the Log_e (screening values)
 x - screening values over which the integration is being done
 CF - cumulative function described above in lbs/hr.

The form of the cumulative function can be simplified by algebraic reduction and change of variables to obtain.

$$CF = C(10)^{B_0} \exp \left[-\frac{u^2 - (u + B_1\sigma^2)^2}{2\sigma^2} \right] \Phi \left[\frac{\text{LOG}_e (S_0) - u - B_1\sigma^2}{\sigma} \right]$$

where Φ is the cumulative function of a standard normal distribution.

This function was used in developing the cumulative emissions function shown on the nomographs. The censored distribution parameter estimates described in Section A.4.2 were used for the lognormal distribution parameters in each case except compressor seals. The Log/Log least-squares regression estimates described in Section A.4.1 were used for the scale bias correction factor and for B_0 and B_1 .

The scale for the above cumulative function is in lbs/hr. To obtain a cumulative percent function, the number obtained in lbs/hr at each screening value was divided by the value of the function at a screening value of one-million ppmv. This forced the cumulative function to 1.0 at one-million ppmv. These scaled values were then subtracted from 1.0 and multiplied by 100.0 to obtain the functions shown on the nomograph.

The estimated cumulative emissions functions were compared with the sample functions and found to adequately approximate the data in most cases. Again, the biggest discrepancies were near the 10,000 ppmv screening value where the sample function has a big jump. This area is more critical for this function than the cumulative distribution function since most of the emissions are attributable to sources with screening values greater than 10,000 ppmv. It is important to note that very little screening data is available with screening values greater than 10,000 ppmv. Thus, this portion of the curve is based on extrapolations using models developed from screening values less than 10,000 ppmv.

This cumulative function is a very complex nonlinear function of five sample statistics:

- (1) the intercept and slope from the regression of Log leak rate on Log screening value,
- (2) a bias correction factor used when converting the logarithmic to the linear scale, and
- (3) the mean and variance of the natural logarithm of the screening values.

Due to the complexity of this function, it was not possible to derive a closed-form analytical expression for the confidence intervals. Thus, a Monte-Carlo computer method was used to generate the confidence intervals.

This method involved regenerating the cumulative function 400 times. Each time, the data collected in the project (the exact number of sources with screening values greater than zero) were regenerated, except with an independent set of random variations. The distributional properties of the leak rate and screening data were used in computing the required random numbers.

For each of the 400 trials, sample estimates of the five parameters required to compute the cumulative function were computed. Then these estimates were used to generate a new cumulative function. The five percent lower result and the five percent upper result from the 400 trials for any given screening value were then selected as the 90% confidence limits for the population cumulative function. These approximated 90% confidence limits can be interpreted as follows:

When we state that the true percent of total emissions, for the population of sources, attributable to sources with screening values greater than a selected valve, is within the confidence bounds, we expect to be correct about 90% of the time.

Since these confidence limits address the uncertainty in the cumulative function for the entire sampled population of a particular source type, they are not necessarily applicable to a finite sample of sources in a particular situation. The variation of this function depends on the number of sources in a complex manner, so it is not possible to draw a general conclusion for the effect of sample size. Monte Carlo simulation techniques can be used to approximate intervals for a finite random sample of a particular source type.

As an example, Figure A-5 shows the confidence intervals for the cumulative percent of emissions functions for valves in light liquid/two-phase service. Intervals are shown which are applicable to a random sample of 100 valves and a random sample of 1000 valves. Also included are the confidence intervals for the entire population (from Figure 4-8A). As can be seen, the intervals applicable to a finite number of sources are significantly wider than those for the population.

These intervals for finite populations were also developed using simulation techniques. Four hundred Monte Carlo trials generating 100 sets of data and 400 trials generating 1000 sets of data were run. In each of the trials, the generated sample was ranked according to screening values and a sample cumulative leak rate function computed. Each sample function was scaled by dividing by the total leak rate generated. Then the five percent lower result and the five percent upper result from the 400 trials for any given screening value were selected as the 90% confidence bounds.

These confidence intervals can be interpreted as follows:

When we state that the cumulative percent of total emission function, which would be generated from a random sample of "m" sources, will fall within the confidence bounds, we expect to be correct about 90% of the time.

where "m" is the number of randomly selected sources in a particular situation.

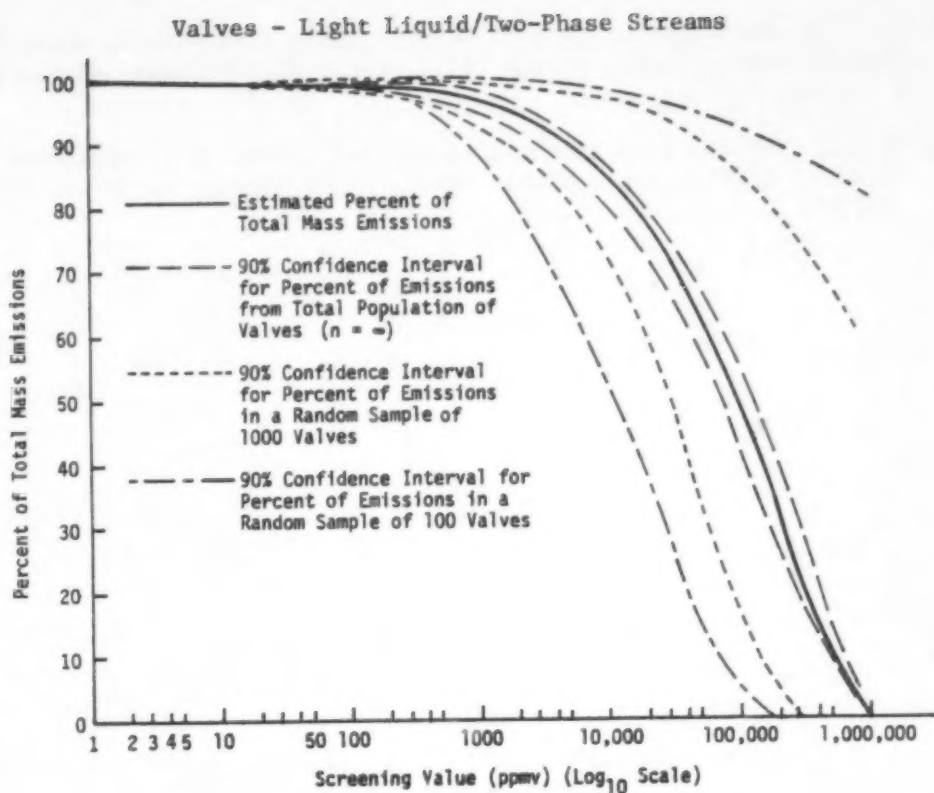


Figure A-5. Cumulative Distribution of Total Emissions by Screening Values - Valves - Light Liquid/Two-Phase Streams - Comparison of Confidence Intervals

REFERENCES

- Aitchison, J., "On the Distribution of a Positive Random Variable Having a Discrete Probability Mass at the Origin", American Statistical Association Journal, 50, (9), 1955, 901-908.
- Cohen, A.C., Jr. "Simplified Estimators for the Normal Distribution when Samples are Singly Censored or Truncated", Technometrics 1, (1959) 217-237.
- Finney, D. J., "On the Distribution of a Variate Whose Logarithm is Normally Distributed", Journal of the Royal Statistical Society, Series B, 7 (1941), 155-161.
- Patterson, R. L., "Difficulties Involved in the Estimation of a Population Mean Using Transformed Sample Data:", Technometrics 8, No. 3, (1966), 535-537.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

CINCINNATI, OHIO 45268

DATE: APRIL 30, 1979

SUBJECT: Report(s) for Inclusion in NTIS

FROM: Gilbert M. Gigliotti *G.M. Gigliotti*
Director, Technical Information Staff

TO: Input Branch
National Technical Information Service
U.S. Department of Commerce
Springfield, VA 22161

Enclosed are reports for inclusion in the National Technical Information Service. All required information and forms are included.

If you have any questions or need any other information, please call Ms. Lynn Pretty, Area Code 513/684-7554. Thank you for your cooperation.

TITLE (REPORT NUMBER)

EMISSION FACTORS AND FREQUENCY OF LEAK
OCCURRENCE FOR FITTINGS IN REFINERY
PROCESS UNITS
EPA-600/2-79-044

COPIES

10

cc: W. WHELAN